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THE INSTITUTE OF PETROLEUM

AN Ordinary General Meeting of the Institute of Petroleum was held at 61 New Cavendish Street, London, W.1, on 4 February 1959, the Chair being taken by C. M. Vignoles, C.B.E., President of the Institute.

The General Secretary read the minutes of the previous meeting, which were confirmed and signed as a correct record. He also announced the names of members elected since the previous meeting.

The Chairman introduced the authors, and the following paper was presented in summary:

CONTROL OF MARINE ORGANISMS IN A SALT-WATER COOLING SYSTEM *

By D. H. TULLIS † (Fellow), L. C. NEILL † (Associate Fellow), and A. T. HENDERSON †

SUMMARY

Although provision was made in the design of Coryton refinery for chlorination of the once-through salt water cooling system, this provision had been made primarily for slime control. After commissioning of the refinery, it soon became evident that whilst control of slime formation was adequate, a major problem of controlling growth of marine macro-organisms existed. Literature search into the life and habits of the common black edible mussel elucidated the problem to some degree, and experimental work revealed many interesting facets on the varying requirements of Thames water with regard to chlorination for control of these mussels. This work also indicated that certain modifications to the Coryton refinery cooling water system would be necessary to achieve adequate control of slime formation, growth, and periodic elimination of marine macro-organisms, and removal of silt deposition.

INTRODUCTION

Two types of marine fouling can be encountered in heat exchangers, condensers, and the cooling water circuit. These are:

1. Slime formation.
2. Marine macro-organisms.

Slime formation is mostly due to the accumulation of micro-organisms of the filamentous and capsulated bacteria type, which then traps suspended inorganic matter. The degree of slime formation and stickiness is dependent on the individual type of organism, and suspended inorganic material adheres to the sticky film to form a slime. The deposition is also dependent on the bacterial food material present and the temperature of the water.

The common edible black mussel, *Mytilus Edulis*, has been identified by Clapp [1] as the most important macro-organism in the fouling of equipment and systems using sea water, and as the most difficult to control. Although there are many different types of marine animals and plants which can be classed as fouling organisms, these can be divided into two main groups; those which are incapable of further movement after having become attached, and those which can become secure or change their location at will. Barnacles and algæ can be included in the first group; the second group includes mussels and sea anemones. These in the second group can migrate from an undesirable location and become firmly re-attached in another location where conditions are more favourable for their support. In view of Clapp's identification and researches, and the abundant confirmatory evidence we obtained in fouled equipment, our efforts were directed essentially against the black edible mussel, *Mytilus Edulis*. Fig 1 is a photograph of a 4-inch water inlet line to a naphtha cooler, and gives some idea of the fouling which can result from these mussels, and of the size to which these mussels can grow in an inadequately protected system.

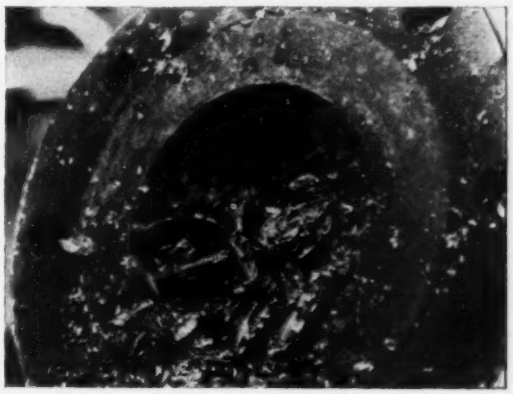

FIG 1

FOULING FROM MUSSELS IN A WATER INLET LINE TO A NAPHTHA COOLER

The edible black mussel normally exists in large

* MS received 30 September 1958.

† Mobil Oil Co. Ltd., Coryton, Essex.

numbers in waters with salinities between 15,000 and 30,000 p.p.m. or more, *i.e.* normal sea water. Where conditions are favourable, and the Thames Estuary appears to provide these conditions, these mussels frequently form great " beds " on the mud flats between high- and low-tide levels. Estimates vary widely, but it appears that the female mussel may produce considerably more than a million eggs in a single season. Cell division and the development of the embryo proceed rapidly after fertilization.

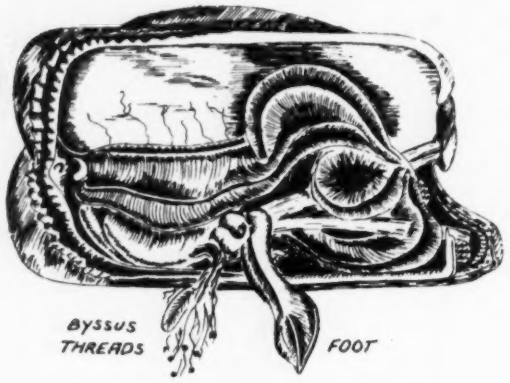

FIG 2
MYTILUS EDULIS

The larva at this stage is free-swimming, and it then attaches itself to a hard surface and develops a single shell, but is still capable of swimming and crawling. Almost immediately after the formation of this first shell a second bivalve shell is developed. The time for the development to the successive stages can vary considerably, environment probably playing an important part. The spawning period depends on the locality, but in the British Isles is usually from June to October.

When the bivalve shell is obtained, a high degree of resistance is achieved, due to the mussel's ability to keep its shell shut for extended periods, thus excluding any toxic matter. When unirritated or in favourable surroundings the mussel's shell is normally open at 15°–20°. An adult mussel is capable of movement, should this become necessary due to a deterioration in the environment, and this is achieved, after the breaking of the byssus threads by which the mussel is attached to the surface, by crawling, using a single foot. The rate of progress can be several feet an hour. Fig 2 is a drawing of the internals of the mussel and indicates the single foot by which movement is achieved and the byssus threads by which it secures itself to a surface.

In addition to this method of locomotion, juvenile mussels of 4–5 mm in length are also able to float, but in this way they have no power over their own movements and are carried along by the water flow until deposited. Conditions beneficial for mussel growth are darkness, continual submergence, and adequate food and oxygen supply. Non-circulating cooling water systems possess all of these qualities in addition to the exclusion of predatory fauna.

Control of Marine Fouling

Although control methods suggested and tried are numerous, the most popular and best known method of control of marine fouling in salt-water systems is chlorination control, and as equipment for this type of control was included in the design of Coryton refinery, all literature research and investigational work was directed primarily towards the use of this method.

Chlorine can be injected into a cooling water system either intermittently or continuously. The economic attraction of intermittent chlorination with regard to chlorine consumption is obvious. The purpose of intermittent chlorination is to destroy the fouling organisms periodically before an appreciable build-up has occurred, and slime control is more readily achieved by this method than control of mussels. The mussel larvæ in an advanced state of development may enter the cooling water system and develop their bivalve shells in between chlorination periods and in addition young floating mussels already possessing their bivalve shells can easily be drawn into the system through the screens. Intermittent chlorination is unlikely to affect other than the larvæ which have not had time to develop their bivalve shells. Published evidence of other than the lethal effect of intermittent chlorination appears to be somewhat conflicting. Hutchins [2] reported that with 20 minutes injection every 8 hours, no killing of adult mussels occurred, and the mussels were fatter than those growing in unchlorinated water, whereas Patten [3] stated that a residual chlorine concentration of 2 p.p.m., injecting for one hour every 8 hours also produced no killing but the average mussel size was smaller.

It is also indicated by Chipperfield [3] that mussels prefer to attach themselves to surfaces which are relatively algæ-free, and this condition is, of course, to be found where intermittent chlorination is employed.

From all published information it appears that continuous chlorination is essential for complete elimination of mussels and thus, where intermittent chlorination is employed, Whitlock [4] contends that this should be supplemented by a variable period of continuous chlorination at a residual chlorine concentration of about 0·5 p.p.m. Mussel destruction proceeds more rapidly by continuous chlorination at higher temperatures, and White [5] states that if the temperature is raised sufficiently destruction occurs without the aid of chlorine. The temperature at which this occurs is dependent upon the locality and

apparently on the average temperature to which the mussels have been accustomed. Patten [3] has reported an annual yield of 331 tons of mussels from a sea-water tunnel, at a plant prior to chlorination. After cleaning and application of intermittent chlorination the yield was reduced by 95 per cent and by more than 99 per cent when using continuous chlorination.

Chlorine Demand

In solution, chlorine is present as hypochlorous acid or as the hypochlorite ion and not as molecular chlorine. Chlorine present in this way is termed the free residual chlorine. Chlorine may also combine with some substances but still be in an available form. This is termed as combined available chlorine, and is further mentioned below. The total available chlorine is the sum of the free residual and combined available chlorine.

A variety of substances in water react with chlorine, resulting in its complete removal, and the quantity of chlorine consumed in this way is termed the chlorine demand. It is in effect the quantity of chlorine added less the total available chlorine. Among the substances in water which react with chlorine are certain oxidizable metals, inorganic reducing agents, ammonia and amino compounds, and organic compounds. Reaction with inorganic compounds is usually instantaneous, but with organic substances can be very variable. Chlorine demand thus varies with contact time, and often with the chlorine dose applied, which aspects are discussed later and vary widely for different waters.

Nitrites and hydrogen sulphide both react with chlorine. In the case of H_2S one part of H_2S reacts with 8·5 parts of chlorine; thus only a small amount of H_2S, hard to detect by normal analytical procedure, can raise the chlorine demand appreciably. Ammonia and amino compounds can react with chlorine to form chloramines in which the chlorine atoms are available, but further chlorination tends to oxidize ammonia to nitrogen.

In the iodine method of determining total available chlorine no differentiation is made between free available chlorine and chlorine contained in chloramines. Free available chlorine is, however, much more effective for bacterial destruction than chloramines.

Destructive Action of Chlorine

The action of chlorine was thought to be due to complete oxidation of the organism. However, it is reported by Fair [6] and Green [7] that as the lethal concentration of chlorine required is much less than for complete oxidation, and as other oxidizing agents fail to produce similar results, it appears that a selective attack on a vital part of the cell occurs. It is considered that an essential enzyme is attacked, and that this enzyme is probably triosephosphate dehydrogenase, the attack taking place on the –SH groups. The small size of the HOCl molecule is also thought to be a factor in permitting passage through cell walls.

CORYTON CHLORINATION PLANT AND COOLING WATER SYSTEM

Description of Plant

The chlorinator is a Wallace and Tiernan master visible vacuum type with a maximum continuous rating capacity of 250 lb/hr.

The operating cycle as designed consists of:

(*a*) A priming period when chlorine-free water passes through the injector and the chlorine solution piping to obtain uniform hydraulic conditions for the ensuing chlorination period.

(*b*) A chlorination period, when the chlorine is metered as a gas under vacuum and is absorbed in the water passing through the injector to form a chlorine water solution.

(*c*) A flushing period after the chlorine supply is cut off when water passes through the injector and solution piping to remove all traces of chlorine solution, so that when the plant is shut down only chlorine-free water is contained in the solution delivery pipe.

The chlorine water solution, during the chlorination period, passes through the solution delivery piping into a central pit in the water intake caisson and mixes with the incoming Thames water, which then passes on to the separate pump suction chambers.

Injection into the central pit rather than directly into the cooling water lines is preferable, since it also ensures fouling control of the pump chambers and pumps and requires only a simple injection device. Line injection, on the other hand, would require separate chlorine flow control for each individual line, each rate of injection being dependent on the cooling water flow through that particular line.

The room housing the chlorinator is kept at 10° F above the temperature of the chlorine drum room to prevent the formation of chlorine hydrate, which occurs when the gas expands in contact with water at too low a temperature.

The Cooling Water System

The original design and layout of the entire cooling system is shown schematically in Fig 3 and was based on two completely separate sections with only one common point, namely, the suction of all pumps. It is into this common suction that chlorine injection takes place. The water is drawn from the River

Thames and has an average salinity of *ca* 20,000 p.p.m. as sodium chloride. The cooling systems are as follows:

Process cooling (operating units) is at 52 p.s.i.g. and by two lines from pump house at water intake,

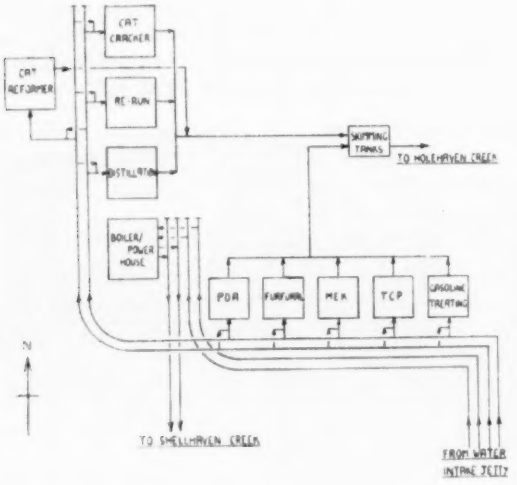

FIG 3

CORYTON COOLING WATER SYSTEM

starting with 42-inch diameter lines and gradually reducing through stages to 24-inch diameter as unit offtakes reduce quantity flowing.

Installed pump capacity is 37,500 g.p.m., made up of two 650-h.p. electric-driven pumps and one turbine driven standby. One electric pump is connected direct to each 42-inch line, the turbine-driven pump being common to both lines. Process cooling lines terminate in blanks at the North end.

The *power station cooling* system is identical in conception, except that all pumps are 200 h.p. at 37 p.s.i.g. discharge pressure, with a total installed capacity of 16,500 g.p.m. and supply through 36-inch diameter lines. The boiler house and power station cooling system discharges by 36-inch lines to the river, while the refinery process cooling water returns from units through two lines to skimmer tanks and thence to Holehaven Creek. All lines are of welded construction, fitted with expansion joints and bitumen coated internally.

Experimental Work

Up to September in the year in which these investigations started, chlorine injection was generally at the rate of 2½ lb/min for 12 minutes every 4 hours, this being the recommended dosage for slime control. There had, however, been many occurrences of fouling of tubulars by mussels, two typical examples of such fouling being shown in Figs 4 and 5. Consequently, chlorine injection was changed to 50 minutes every 8 hours, the dose rate remaining the same at 2½ lb/min. This dose rate was equivalent to about 12 p.p.m., aiming at a total available chlorine content of 2–3 p.p.m.

Subsequent total available chlorine checks from the pump discharge at the water intake showed maxima varying between 3·0 and 0·75 p.p.m., and the value obtained appeared to be dependent on the state of the tide at the time of injection. A selection of results is shown in Fig 6, total available chlorine being plotted against time after start of injection. The

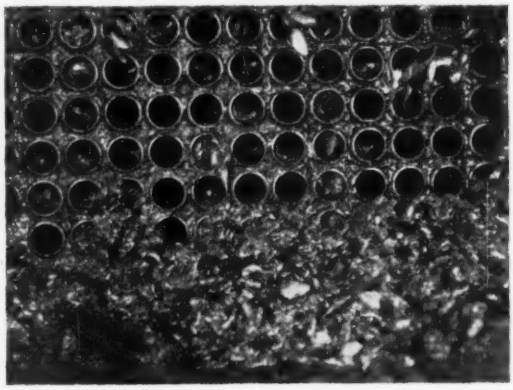

FIG 4

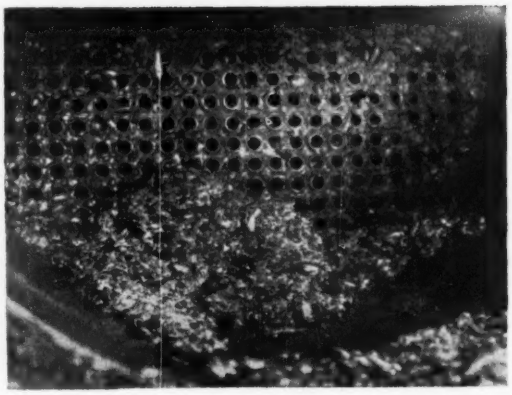

FIG 5

total available chlorine of the outfall water after use followed the same trend as that of the intake water; time intervals between intake and outfall plots correspond to the time of travel through the cooling water system.

A composite plot of the maxima total available chlorine results against time in relation to high tide (Fig 7) showed that the highest maxima were obtained when injecting chlorine at high tide.

It was considered that the variation in the total available chlorine content was probably due to variations in the chlorine demand of Thames water. As a confirmation of this view, a chlorine demand survey of Thames water was carried out in the following month, October, when the water temperature was 58° F.

The results of this survey are shown in Fig 8, indicating a minimum chlorine demand of 3·3 p.p.m.

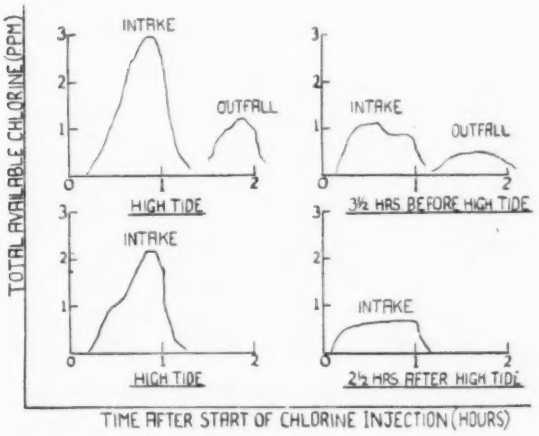

Fig 6

TOTAL AVAILABLE CHLORINE AT WATER INTAKE AND SHELL HAVEN OUTFALL FOR 50-MINUTE CHLORINE INJECTION PERIODS

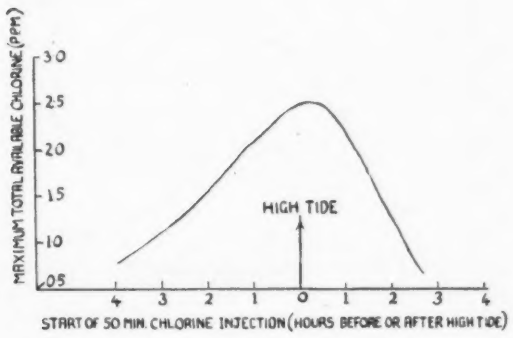

Fig 7

MAXIMUM TOTAL AVAILABLE CHLORINE AT WATER INTAKE. CHLORINE INJECTION AT VARYING STATES OF TIDE—SEPTEMBER

at high tide and a maximum of 7·5 p.p.m. about two hours before low tide. Accordingly chlorine injection was changed from 50 minutes every 8 hours to 50 minutes at every high tide, with saving in chlorine cost and increase in effective use.

Demand v. *Dosage*

The above survey of chlorine demand was carried out with excess chlorine concentration to ensure that demand was independent of dosage. As reaction

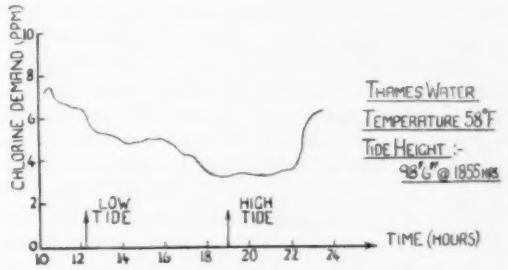

Fig 8

CHLORINE DEMAND OF THAMES WATER AT CORYTON—OCTOBER

with organic substances in the water can be variable, this was checked by determining the effect of varying dosages on bulk samples of Thames water taken at low and high tide. Total available chlorines were estimated after 30 minutes contact time (the effect of contact time will be discussed later).

The results obtained are plotted in Fig 9. Again the greater demand at low tide is shown, and it will

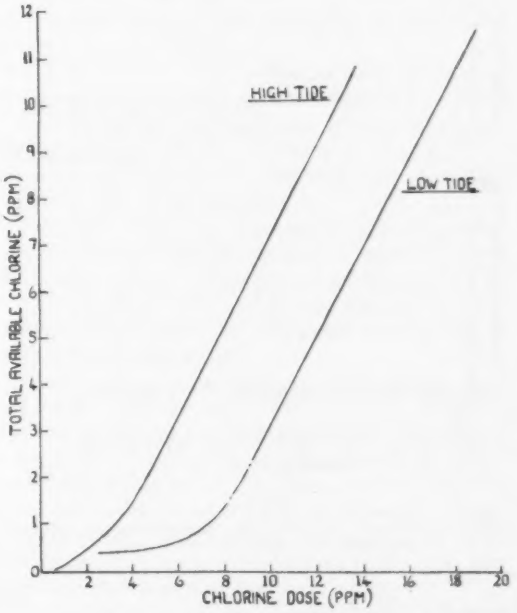

Fig 9

VARIATION OF CHLORINE DEMAND OF THAMES WATER WITH CHLORINE DOSAGE

be seen that above certain dosages total available chlorine increases by the same amount as increase in dose, *i.e.* chlorine demand is then independent of dosage.

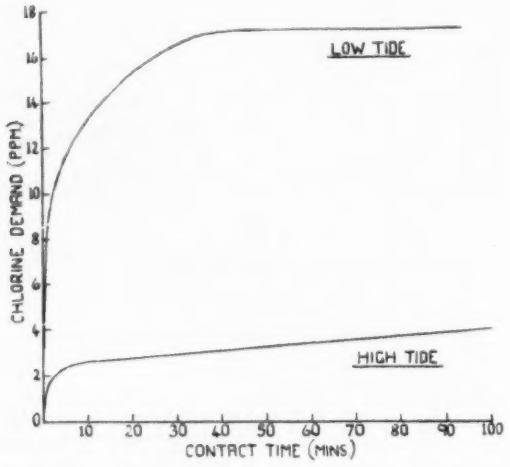

FIG 10

CHLORINE DEMAND OF THAMES WATER. VARYING CONTACT TIME OF CHLORINE SOLUTION

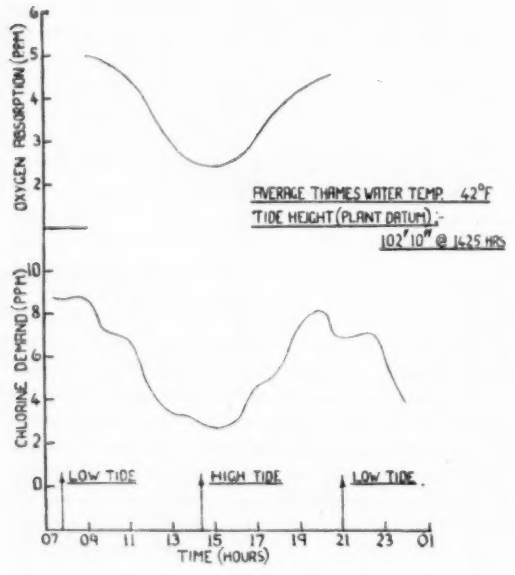

FIG 11

CHLORINE DEMAND AND OXYGEN ABSORPTION OF THAMES WATER AT CORYTON—FEBRUARY

Demand v. *Contact Time*

Initially, 30 minutes contact time was chosen for the demand survey as being representative of the

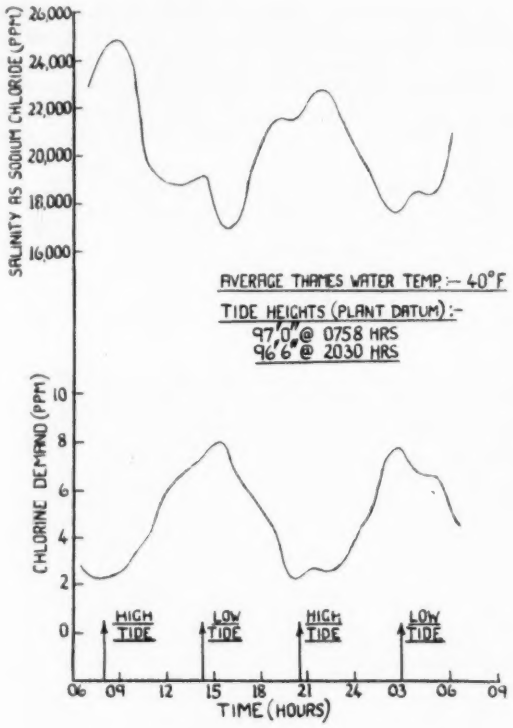

FIG 12

24 HOUR CHLORINE DEMAND AND SALINITY SURVEY OF THAMES WATER AT CORYTON—FEBRUARY

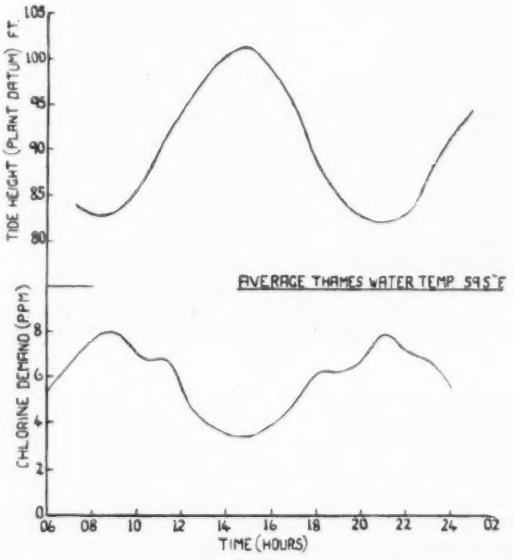

FIG 13

CHLORINE DEMAND SURVEY OF THAMES WATER AT CORYTON—JUNE

average time taken for the injected chlorine to reach coolers in the refinery. An investigation of the effect of contact time on chlorine demand, dosage always being in excess, is demonstrated in Fig 10. It may be seen that at 30 minutes the reaction has very nearly reached completion and the rate of chlorine consumption is slow, so that at this stage small errors of timing have a negligible effect on chlorine demand.

Having established a general pattern of chlorine demand, it was desirable to redetermine at intervals to find the effects, if any, of seasonal and other changes on chlorine demand. The results are given below in Figs 11–14.

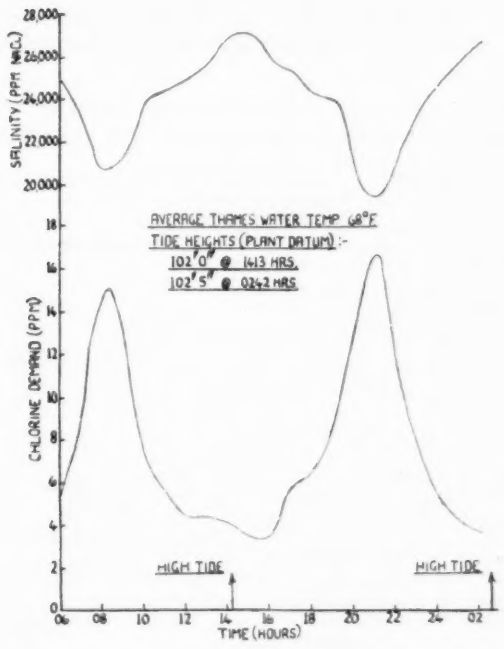

FIG 14

CHLORINE DEMAND AND SALINITY SURVEY OF THAMES WATER AT CORYTON—JULY

As tide heights are quoted or shown graphically it is appropriate here to quote tidal variations.

	Coryton Plant datum, ft
Mean high water:	
Spring tides	101·1
Ordinary tides	99·6
Neap tides	97·8
Mean low water:	
Neap tides	86·2
Ordinary tides	84·7
Spring tides	83·3

100 ft plant datum = 8·5 ft Newlyn datum.
= 10·0 ft Liverpool datum.

The survey in the following February (Fig 11) covered a high tide of 102·8 ft, and thus the rise and fall of water level was rapid. The water temperature was 42° F, and the maximum and minimum chlorine demands recorded were 8·7 and 2·7 p.p.m. respectively. Samples taken for oxygen absorption over part of the survey showed a maximum of 5 p.p.m. and a minimum of 2·5 p.p.m., coinciding with the times of maximum and minimum chlorine demand. With the incoming tide after low water, much silt was suspended for a short period, and the chlorine demand then rose slightly, as shown by the minor peaks at 10.30 and 22.45 hours.

On 17–18 of the same month, when the Thames water temperature was 40° F, a 24-hour survey was carried out (Fig 12), during which salinities were also determined. The tide heights were 97 and 96·5 ft, and excessive turbidity of the water, which coincided with minor peaks in the chlorine demand curve earlier in the month (Fig 11), was absent. As might be expected, the change in chlorine demand appears to be more gradual with smaller rise and fall of the tide.

It may be noticed that the minimum salinity coincides exactly with maximum chlorine demand and that maximum salinities were observed just after high tides. This, together with the coincidence of minimum chlorine demand and minimum oxygen absorption at high tide, demonstrated in the previous survey (Fig 11), is ascribed to the influx of clean sea water into the Thames estuary at high tide, compared with the relatively polluted river water flowing downstream with a falling tide.

Prior to the survey in June, a tide gauge had been installed and a plot of tide height is also given in Fig 13. To be noted is the greater minimum chlorine demand of 3·5 p.p.m. (*cf* 2·5 p.p.m. in February), probably due in part to greater reactivity at higher water temperatures.

One other point noticed during this survey was that the water contained suspended matter, which coloured the Thames brown. Filtering through a sand filter in general reduced the chlorine demand slightly, but the results tended to be erratic, and no further importance was attached to this aspect.

A final survey was carried out during 20–21 July during a hot weather period when the river temperature was 68° F and the high tide height was 102 ft. It can be seen (Fig 14) that, although similar to the other summer and autumn surveys over the high tide period, with a minimum of 3·3 p.p.m. chlorine demand, it differs considerably over the low tide region, with chlorine demand rising to as high as 16·5 p.p.m. and coinciding with a time of minimum salinity.

This graph in particular illustrates the futility of chlorine injection at low tide.

It was in this month, as a result of the above surveys and a further occurrence of mussel trouble, that

injection during the summer mussel breeding season of May–October was increased to two 50-minute periods, one 2½ hours before and the other one hour after high tide. Winter injection remained at 50 minutes at high tide.

A dosage of between 7 and 8 p.p.m. is aimed at, and a total available chlorine content of between 2 and 3 p.p.m. at the water intake is considered satisfactory. The purpose of the chosen double injection during the summer is to leave less time for the development of larvæ entering the cooling water system in between chlorination periods, in addition to increasing the total chlorination period. The timing is, of course, to coincide with the period of relatively low chlorine demand.

The original design of the Coryton cooling water system, which has already been described and shown schematically in Fig 3, had several shortcomings.

For instance, no provision was made for flushing out of the individual intake lines to process units or boiler/power house.

Also, apart from absence of inter-connexions, different pressures and inflexibility of pumping arrangements at the intake precluded interchangeability of boiler house and process unit cooling lines.

Since the commissioning of the refinery in 1953, throughputs have been steadily increased and new units brought on line, resulting in constantly increasing demands for process cooling water to the extent that both lines on this duty are continuously in service, thereby making it virtually impossible to take one line out of service for cleaning even during an annual turn-round of a major process unit. On the other hand, the capacity of the boiler house cooling water system has proved to be more than adequate and even with still greater demands for power and process steam in the future, with turbo-alternators of the passout/condensing type, one cooling water intake line will suffice. With the lower demand situation on this system, it has been possible to isolate one boiler house cooling line at a time for cleaning, with makeshift arrangements for flushing. At one such clean-out heavy silt deposit was found to extend for a distance of 15–18 ft from the blank end. It has also been possible to carry out static chlorination tests on this system, which indicated that a 100 per cent kill of mussels growing within the line can be achieved.

Consequently, after completion of the chlorination investigation, increasing awareness of mussel growth, and evidence of silt deposition, it was decided that some modification to the cooling water system was imperative to allow static chlorination and full-bore flushing to be carried out. To install a third line would be expensive in that double-decking of line would be necessary because of lack of space in the pipe-track and, again, space at the intake caisson is severely restricted. Since, as explained, one boiler house cooling line is adequate, it was decided to carry out the following line modifications, which are shown in Fig 15:

(i) Cross-tie the two process cooling lines with one boiler house cooling line as indicated at point A, so that this boiler house cooling line can serve either boiler house or the process units involved.

(ii) Inter-connect the two process cooling lines at their Northern extremity, point B, and provide a connexion to drain.

(iii) Cross-tie the two boiler house intake lines with one of the effluent lines, as indicated at point C.

By this means it will be possible to take out of service any one intake line, static chlorinate this line for a

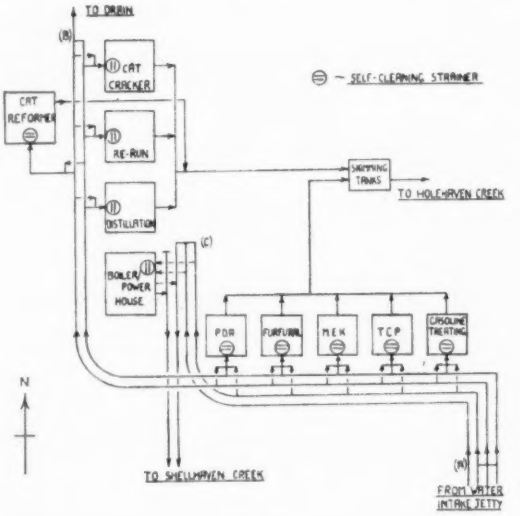

FIG 15

CORYTON COOLING WATER SYSTEM—MODIFIED

period of 7–10 days, and then flush out at full bore. It is anticipated that static chlorination and flushing will be necessary every two years, with full-bore flushing every year for silt removal. Static chlorination will be conducted during August so as to take full advantage of seasonal climatic conditions to achieve a maximum temperature in the static line and thus assist the percentage kill of mussels.

One further modification to the cooling water system, which is depicted in Fig 15, is the provision of self-cleaning power-operated rotary filters. The justification for these stems from past experience with locally fabricated filters with back-flushing arrangements, which were installed at each plant after the first experiences of fouling of tubulars. These "home-made" filters were successful, up to a point,

but when a change in velocity in an intake cooling line took place for one reason or another, the manual cleaning and change-over of these filters was excessive for up to 24 hours. In addition, failure of individual tubes in condenser bundles was very frequently encountered, quite apart from the increase in pressure drop associated with tube-plate fouling. Such tube failures were in the majority of cases the result of impingement arising from a partial blockage of the tube by a mussel shell. Quite apart from the gains expected in cooling line operations from periodic static chlorination and line flushing, experience indicates that such protection as efficient filter devices can offer is essential for cooling equipment within plant battery limits.

ACKNOWLEDGMENTS

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DISCUSSION

J. R. Baddiley: This paper deals with an interesting and essential aspect of an indispensable refinery facility. It illustrates the economic advantages to be secured in dosing chemicals by studying natural conditions.

When we read this paper at Fawley we were surprised to note the similarity of natural conditions at Fawley and Coryton and also in the installed facilities to counteract difficulties with marine organisms in the salt-water cooling system.

Our experience, particularly in respect to mussel fouling of pipelines, has, however, been directly opposite to the experience at Coryton.

In respect to natural conditions, our intake is from Southampton Water, which has a normal temperature range between winter and summer of 43°–68° F and a tide variation of 10 ft. Our salinity is also similar and about 19,000 ppm NaCl. Our average low tide chlorine demand is 5 ppm.

We chlorinate by using similar equipment to that at Coryton, but do not make any special effort to correlate dosing time with tidal conditions, due partly to the complexity of the tides in the vicinity of Southampton Water. We do feel, however, that intermittent rather than continuous chlorination is essential.

The only time mussel fouling has been encountered at Fawley was in 1946 when the old refinery started up after the war. It was found that mussel growth had developed in the system during the few years the refinery was shut down. However, the mussels died in the static system and the resultant dead material was washed through the system to the sea.

When the new refinery started up in 1951, with a refinery process water flow of about 50,000 U.S.gpm, as it then was, a dose similar to Coryton of about 10 ppm was applied. Dosage has been carried out with varying frequency, but generally for about one or two hours per 8-hour shift.

Despite the increased process water flow, now approximately 100,000 U.S.gpm, no mussel trouble whatever has occurred, even though mussels can be seen attached to the jetty piles. Could this be anything to do with the depth of the water intake below minimum water level? At Fawley this is 8·5 ft, the maximum being 18 ft. Perhaps the authors would comment on the Coryton intake.

The only marine contamination encountered at the present time at Fawley is due to a type of acorn barnacle and to a type of seaweed.

The acorn barnacle is similar to the mussel in that it can close up for periods in toxic conditions. It attaches itself in places where there is turbulence and aeration of the water, *e.g.* at pipe bends. It can penetrate bitumen lining, but has no effect on concrete nor does it stick to Neoprene lining.

In our experience, these barnacles are not troublesome in that they do not penetrate into the salt-water cooling system far enough to reach the bitumen-lined piping which begins 2600 ft downstream of the intake. The first 2600 ft is Neoprene-lined on one 60-ft supply line. The other 60-ft line is cement lined for the total length, which is about 7000 ft in both cases.

Seaweed contamination is the main problem in our system. An authority on marine growth was consulted as to whether this weed originated in the sea or within the refinery cooling water system. He identified the seaweed as the type *griffithsia* with some *heterosiphonia plumosa*, both being members of the group *Rhodophycaea* —red algæ, which comes into the system from the sea. Chemical treatment is thus useless, as the seaweed dies in the system anyway. The problem is, therefore, one of improved filtration.

Process water at present passes through ¼-inch mesh band screens in the main pump suctions and, in addition, through ½-inch mesh strainers on each block. Despite this, weed gets through and clogs ½-inch tubular equipment.

Investigations are being carried out in order to find more effective types of straining media which will prevent ingress of the weed to tubular equipment. No results have yet been obtained.

It is reported that ultrasonic vibrators have been successful in eliminating problems of this sort, and the possible application of the technique in this instance is being considered.

At Fawley there is a further problem which relates to organic contamination of salt-water cooling systems. This is bacterial contamination of effluent water in the sewer system. Bacteria growing in the sewer system are carried down to the separators where they collect and clog the skimmers during skimming operations. It is probable also that they reduce the efficiency of oil/water separation by forming an agglomerate with oil and silt of about unit specific gravity.

Our consultant considers that these bacteria are probably a recurrence of *bacillus cereus* and *bacillus mycoides*, which caused similar trouble in 1951. These

bacteria originate in soil and in mud flats near the sea, but can exist and propagate in the favourable conditions of the refinery sewers, *i.e.* darkness, warmth (~90° F), and the presence of nutrition in the form of hydrocarbons, especially unsaturates.

We have been advised that the presence of chlorine, chlorite ions, copper ions, or cuprammonium ions would inhibit their growth. Dosing cuprammonium ions at strategic points around the sewer system is being tried, but as yet no significant results have been obtained.

There is the possibility that ultrasonic vibration may also find an application in this problem.

D. H. Tullis: In some respects, we feel almost envious of Fawley when they say they have not had any trouble with mussels. In one other respect, we are glad that we have no trouble from barnacles or seaweed.

On the question regarding the variations in depth, I cannot pass an opinion on whether that is the reason why they suffer from fouling of a different kind. At Coryton the water intake suction point is 6·5 ft below minimum tide level. I am not too familiar with the Fawley and Southampton Water area and I do not know whether they have the same incidence of mudbanks as we have at Coryton. But it does appear that mudbanks encourage the mussels. We have mudbanks comparatively close to the refinery, although, of course, we do have good deep-water berthing facilities.

As far as sewage is concerned with the cooling water system, we did have some difficulties in the very early days of the refinery, but they were due to sewage inadvertently entering the separators. The design was that sewage effluent would not go through the separators, but into a moat which surrounds part of our storage tank area. Once the sewage effluent had been diverted we had no further trouble in the cooling water skimming tanks from that particular source.

F. J. R. Taylor: The CEGB have this problem of marine fouling in about a dozen stations which have a total circulating water flow of some 100,000,000 gph.

I think there is a fundamental difference between the viewpoint of the authors and my own. I take the view, not that one wants to kill mussels, but rather that one wishes to make the conditions unfavourable so that the mussels do not remain within the power station. It is my experience that a chlorine dose of 3 ppm every four hours will keep the system free from mussels. It is, of course, necessary that a screen with, say, $\frac{3}{8}$-inch square holes should be installed to keep out the adult mussels. The Board's biologists have made a very extensive survey of the effect of power stations on marine organisms and have shown that a very large number of species, including the mussel spat, pass through the power station unharmed. It seems to have been previously taken for granted by some biologists that warming the water in condensers would kill off most of the life in that water and even render it sterile. The data which has now been accumulated and is shortly to be published will show that this is untrue.

I would like to speak for a moment about the duration of the spatting season and hence the period at which the system is vulnerable. We have to take into account that the warm water from the outlet culverts may create an artificially warm environment in the immediate neighbourhood which may prolong the breeding season and even extend it throughout the whole of the year. My recommendation would be to chlorinate intermittently throughout the year, with perhaps a reduced rate between the end of October and the beginning of February.

The static chlorination method which is described in the paper offers a very useful solution in the conditions which occur at Coryton. If this method were adopted with base load plant, *i.e.* plant operating 24 hours a day, either an additional culvert or a by-pass would be required and it is unlikely that these measures could generally be economically justified.

R. B. Besley: This interesting and stimulating paper indicates that even refineries and generating stations in the same area, taking their cooling water from the same source, are not necessarily confronted with the same fouling problems and, moreover, the type of fouling varies widely.

In a large refinery in the North-West we have two main cooling systems, one a closed circulation system with fresh-water make-up through a natural draught cooling tower, and the other a once-through system using a brackish stream of variable concentration returned by way of a natural draught cooling tower to source.

With both systems serious fouling at the commencement of the operations some few years ago was experienced, not, however, with marine organisms such as the mussel, but with algæ and kindred growths.

In the case of the fresh-water closed circulation system, gas chlorination was tried, but due to the cooling stream containing up to 200 ppm of sodium sulphite leaking in at times from an acid concentrator, the chlorine was absorbed to form sodium sulphate and sodium chloride, both of which were innocuous to algæ. Copper sulphate was tried, but with the normal pH of the system the copper precipitated as copper carbonate and floated round the system until an occasional acid leak restored the precipitate to the soluble salt and thus assisted algæ destruction.

Up to this time, experiments had been made on a full scale and those not wholly successful released large masses of algæ and kindred growths. These floated round the circulating system and proved extremely troublesome, due to their capacity for consolidation in header boxes of heat exchangers and coolers.

Whilst this experience concerns a fresh-water system, it is submitted that it reinforces what the authors have covered in their paper and that is the question of the high annual cost that can attend upon full-scale experiments involving high concentrations of added chemicals.

Following a lengthy and detailed laboratory trial it was discovered that a new type of organism was liable to thrive and breed upon dead or dying algæ floating around in the system. This was found to be a type of bacteria, and copper sulphate in the stream with favourable pH effected only temporary relief.

Known killers, such as the mercurial and arsenical compounds, were avoided in view of their lethal affects upon human life. It was found that a rapid build-up of chlorine sufficient to absorb the sodium sulphite would need over one ton per day of chlorine gas at an arbitrary concentration of 250 ppm and that this would cost over £12,000 a year. The laboratory-scale trials indicated that a concentration of only 200 ppm, maintained for three minutes only, would not only kill but also disintegrate and dissolve the organisms and new growths would not arise in periods up to 24 hours even in the " prolific " months of warm weather.

Hypochlorite solution with a 15 per cent availability was selected, costing approximately £1000 a year, and this was delivered to a 20-ton capacity rubber-lined tank equipped with a large delivery line capable of passing at the rate of 300 gpm to the cooling flume. During the off-season and the winter months the dosage was reduced, with obvious economical advantages.

In regard to the brackish cooling system, we experienced a growth mainly of algæ and marine weed and it was found that to kill this was not enough. Full disintegration was required and if the growth could be broken up like tea-leaves then it would go through the system without causing undue trouble. Again, following laboratory-scale investigation, a transient and temporary chlorination level of 250 ppm was successful even when applied only for a few minutes. The hypochlorite solution with a 15 per cent availability was dumped into the main suction pits at the cooling water pumphouse and the results were most satisfactory.

In conclusion, I think it is true to say that, given a fundamental approach, marine and microscopic growths need not produce any serious difficulties in normal refinery cooling systems, but the application of remedies at full scale, although proven elsewhere, should be avoided until tried out satisfactorily on a small scale in the particular location. Furthermore, I can agree with the authors that ceaseless vigilance is necessary to eliminate the mass of growth and if the elimination can take place satisfactorily in the early stages the operation is cheap and easy. However, to try to carry out a full-scale attack on a fully-established organism can be both difficult and extremely costly, not only in biocide chemicals but also in operational efficiency.

D. H. Tullis: Mr Besley mentioned how problems could vary in the same parish. He also mentioned a refinery in the North-West, so I am guessing that he has some information about a neighbouring refinery to ourselves, where apparently they do not have the same degree of trouble with mussels. There is one fundamental difference which might answer this question, namely, that our water intake jetty is close to the banks of the river, whereas the intake of the refinery next door is out in the middle of the river. Whether or not that is the reason why we have more trouble with mussels I do not know. I imagine, judging from the mussel beds on the mud flats, that that is a possible answer. I understand that at Fawley they pump from the intake jetty into a tank and use secondary pumps from there into the refinery cooling system. Possibly mussels exist in the primary tank, although not in the lines of the cooling system, but I am not at all *au fait* with the Fawley situation and just put this forward as a possible explanation.

I do agree with Mr Besley, however, regarding vigilance, because no matter how close one's vigilance is, sooner or later one has trouble with tubulars.

G. G. Page: Several of the graphs show maximum chlorine demands an hour or more before low water. Dr Grindley * has shown that the hydrogen sulphide from decomposing organic matter present in the mud on the bottom of tidal estuaries is liberated over a short period of the tide, with a maximum about one hour before low water. This is attributed to the influence of cyclic hydrostatic pressures holding the dissolved gases in the mud, and gas evolution is shown to be greatest at spring tides.

Regarding the reported variations in fouling between different refinery intakes, I would point out that the larval stages of marine organisms tend to be light sensitive and they are inclined to surface or fall to the bottom according to light intensities, and the level of the intakes, especially in polluted estuaries, may significantly alter the chances of fouling.

The free living larval stages of most marine organisms are extremely selective on the nature of the substrata upon which they settle and they do tend to keep moving about, sounding the substrata until they find a suitable substratum to settle upon. Very small variations in substrata conditions may cause them to keep moving and could account for the variable results reported.

The colonial tendencies of marine organisms should also be mentioned. Once fouling occurs there is a tendency for further larvæ to settle preferentially in the immediate proximity of the adults, and one therefore gets concentration around the initial areas of fouling.

In a lighter vein, I would mention that an American paint firm did attempt to develop an anti-fouling paint on the theory that decomposing organic matter is toxic to the adult and they utilized the decomposition product of crushed mussels removed from a power station culvert. They reported very satisfactory initial results, but these were not substantiated by later trials.

Regarding bacterial and algal films, these often actually develop *in situ* on the surface of the tube, and whilst there has been a lot of work done on the copper leaching rates of the different non-ferrous tubes, service experience would tend to show that these theoretical values are of little practical importance, as once scaling occurs copper leaching falls to a very low rate. The development of slimes is not always detrimental to the corrosion performance of the tubes, although they will cause loss in heat transfer efficiency. There is some evidence to show that organic films can be beneficial to the performance of tubes and I have lately investigated a failure in which it was shown conclusively that the early satisfactory performance of the unit was solely due to the presence of a heavy bacterial slime.

I would agree with the previous speaker on the desirability of small-scale tests and would stress a preference for carrying them out *in situ*. Modified conditions can radically alter the performance.

With regard to the discussion on the use of high chlorination and the possibilities of corrosion, I would like to mention that we have from time to time seen corrosion of non-ferrous tubes used in waterworks. In some cases they heavily chlorinate a small proportion of the flow and pass it through a heat exchanger prior to injecting it into the mains supply to give the required chlorine residual. This procedure has at times caused very severe corrosion of the tubes and we have come to recognize a characteristic form of chlorine corrosion.

Regarding the spatting season referred to by the authors, I would mention that all the mussels in one area tend to spat at the same time, but the time of year can be very variable, depending on water conditions.

The authors mentioned that the fouling tends to develop in the flow path; this is not confirmed by my own observations and Figs 4 and 5 show what I should regard as typical growth which occurs in the areas of eddies. In heat exchangers one normally gets growth on the outlet portions of the tube plate; in pipe bends the growth is normally on the inside of the bend (*i.e.* out of the flow stream).

With regard to the chemical treatment of water, mention has been made of ammonia. I would point out that this could be detrimental in certain circumstances, as it may cause trouble in the non-ferrous heat exchanger tubes.

A. T. Henderson: There is no appreciable decrease in power demand after a line has been cleaned. An

* Grindley, J. *Dock & Harbour*, July 1955, 79.

increased or decreased demand is not discernible on the ammeter, or in any meter which shows the flow.

The initial fouling within the 42-inch lines was to a depth of about an inch and a half, when the line was opened for inspection before we chlorinated and flushed through. There still seemed to be quite sufficient line pressure before flushing and there was no appreciable change in pressure drop after flushing. We did not go to the trouble of putting in any specially accurate gauge. We just used the ordinary tube gauge.

The only thing we do know definitely is that when we did flush out after static chlorination we cleared something in the nature of 6 to 10 tons out into the pipe track drainage area, in silt and mussel shells. This was calculated on the spread-over area by the depth of deposit, plus what went into the moat drainage systems.

L. C. Neill: It would seem that each contributor has his own particular problems as regards control of marine organisms, and even if it is decided that chlorine should be used, quite a few different chlorine demands have been shown up. Although we ourselves at Coryton have a maximum normal chlorine demand in the region of 8 ppm, Fawley's normal low tide chlorine demand was stated to be 5 ppm, which shows there is a difference in the quality of the waters. The Central Electricity Authority chlorinated at 3 ppm, so presumably the chlorine demand of their water in that particular case was below 3 ppm. Having done all these various chlorinations with varying demands, I think we are all perhaps looking for the same thing, which is a total available chlorine in the order of 3 ppm, which, when it gets up to our tubulars, is perhaps 2 or even 1 ppm. That is a very small quantity of chlorine and I do not think we could ever say that we were getting any corrosion from that amount. In using the salt cooling water itself, of course, we do have a problem of corrosion and generally we have gone in for aluminium brass tubes with aluminium bronze tubesheets. Floating head ends have a homogeneous lead lining and the gasket edge has a stainless steel plating, as lead would be extruded. The channel head again has both the division plate edge and the gasket edge plated with stainless steel, and in the channel head box we do apply, to protect the steel in that region, an impressed current of the order of 100 mA to the square foot.

F. J. R. Taylor: We have not had any experience of corrosion which could be directly attributed to chlorine. The tube methods are, of course, picked to suit conditions, and they seem to stand up to it very well.

However, there is an interesting point that one does find corrosion of the cast-iron water boxes of condensers. It certainly seems to have occurred at the same time that we began chlorinating and perhaps putting more power stations near the sea.

There is a theory that the chlorine may well stop the deposition of calcium carbonate, even only a fine film, which would otherwise act as a protective on the water box. In any case, this corrosion can be knocked out by impressed currents or cathodic protection in one form or another. I do not think there is anything that we have been able to directly attribute to chlorine.

E. D. Dolan: Although the paper is on macro-organisms, I would like to ask a question on micro-organisms. The Thames is a notorious breeding ground of sulphate-reducing bacteria. Have the authors found any evidence of the presence of aggressive sulphate-reducing bacteria in their cooling water, particularly at low tide, and if so, does chlorination reduce the aggressiveness?

A second question: the cooling water mains mentioned are made of steel, they are laid on the surface in a pipe track, and are lined with bitumen. What is the velocity in the mains, and do the marine organisms tend to cause breakdown of the bitumen lining? In my experience, acorn barnacles are extremely destructive to soft organic coatings, but I have no knowledge of the effect of mussels.

If the bitumen lining proved satisfactory in service, would the authors give details of the surface preparation of the steel before applying the lining, the type of bitumen, and the finished thickness of the lining?

The effect of cathodic protection on the graphitization of cast iron has been mentioned in the discussion. I know of one instance where a cast-iron water box continued to graphitize in spite of having what appeared to be fully adequate cathodic protection.

It seems that if a graphitized layer (a conducting layer) is once allowed to form, then it functions as an electrical shield. The graphitized layer receives protective current and a calcareous deposit forms, but the protective current does not penetrate to the underlying metal. A galvanic couple exists between the underside of the graphitized layer and the base metal and further graphitization can proceed.

It appears that cast iron which has started to graphitize may not obtain full benefit from cathodic protection unless all graphitized material is first removed.

We have had an experience of the effect of locally favourable conditions on marine growth. Exceptionally heavy barnacle growth in a Scottish loch led to rapid breakdown of bituminous coatings on jetty piles. A marine biologist was consulted and concluded that the water temperature in the loch was some 2° F higher than in the Clyde Estuary, on to which the loch opened; the slightly more favourable temperature conditions encouraged marine growth in the loch.

When a system is designed with facilities for control of marine growth, it is most important that these facilities are operative when the system is commissioned. Otherwise the initial free growth can be very troublesome when it is killed by the eventual operation of the control facilities.

D. H. Tullis: Regarding sulphate-reducing bacteria, we have had no evidence of that at Coryton, although I do know that there has been ample evidence of it farther up the Thames, which has given rise to the atmospheric pollution problems at one time or another.

In regard to the breakdown of bitumen lining of our lines, we have had no experience of this.

A. J. Henderson: Mr Dolan asked about the velocity, which is roughly 3 feet per second. Small pea-sized barnacles have been found attached to the lining. These do not seem to grow to any size, are soft after static chlorination, and can be easily crushed by the slightest pressure.

The thickness of the asphaltic lining is about $\frac{3}{16}$ inch, but we have no idea what it is made of because the pipes came in lined from the suppliers, who also sealed the lining up after the pipes had been welded. There is no visible deterioration of the lining to date. After one flush-out we entered the 24-inch line at one end, as far as it was possible, and we even found the original white paint lines still on the bitumen, which the makers had put on while lining the pipes. I do not think there is any fear of the lining being punctured at any time, since to date there is no sign of this happening.

D. H. Tullis: I must admit that we have learned a lot tonight, in spite of the amount of work we have done on

the control of mussels. I was certainly interested to hear of the success of re-circulation. We could re-circulate a number of our coolers and condensers, but our problem has been to control the growth of mussels in the influent lines and, as these are bitumen-coated, we have not been able to consider the circulation of the hot effluent water back down an influent line.

I must certainly express my gratitude for the information which has been passed on tonight, and I am quite sure it gives us an even better understanding of the problem we have had for a number of years. It is still with us, we have not entirely solved it, but we now have some degree of control over it, and with some of the information provided tonight, we can improve the control that we have already obtained.

The meeting closed with a warm vote of thanks to the authors.

IP TANK THERMOMETERS

In view of difficulties experienced in Great Britain in obtaining thermometer cane suitable for use in the manufacture of thermometers conforming to IP specifications 48 to 51 C and F and 53 C and F, the following modifications have been agreed by the Sub-Committees and Panels concerned to come into force immediately:

(1) Bulb length to be increased from 10–15 mm to 10–18 mm.

(2) Scale length to be increased from 210–230 mm to 210–240 mm.

THE MOLECULAR STRUCTURE OF HEAVY PETROLEUM COMPOUNDS*

By A. HOOD,† R. J. CLERC,‡ and M. J. O'NEAL‡

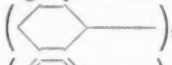
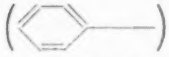
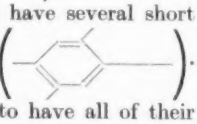
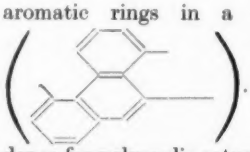
SUMMARY

Mass spectral evidence is pointing toward a new and simple picture of the molecular structure of heavy petroleum compounds. According to this picture, the molecules consist of one long carbon-atom chain, at one or possibly both ends of which a ring system or short branch may be attached.

INTRODUCTION

THERE seems to be a general belief that as higher and higher boiling ranges of petroleum are considered, the molecules rapidly become more complex. This belief is probably a logical consequence of the increase in the number of theoretically possible isomers with molecular weight and of the difficulty of separating compounds or compound types in the higher boiling petroleum fractions.

However, from mass spectrometric studies of the heavy distillate portion of petroleum (*e.g.* C_{20}–C_{40} oils and waxes) during the past several years, another idea of structural composition is coming more and more apparent. Instead of the usual complex picture of molecular structure for heavy oils, mass spectral evidence is pointing towards a new and simple picture of relatively few isomeric molecules making up the predominant portion of any hydrocarbon type at any given carbon number or boiling point. This is in agreement with the gasoline-range distribution of isomers reported by Rossini,[13] and therefore it appears that a single picture of structure applies to the entire distillate range of petroleum.

The new picture is this: the molecules contain essentially one long carbon-atom chain, to one or both ends of which a ring system or short branch may be attached. In paraffin waxes the molecules are predominantly *n*-alkanes (————) along with some slightly branched *iso*alkanes (>————), *cyclo*alkanes  , and even traces of aromatics  . In lubricating oils, the *iso*alkanes have slightly longer branches , and the mono-*cyclo*alkanes and monoaromatics have several short (*e.g.* methyl) branches on the ring  . Polyaromatics generally appear to have all of their aromatic rings in a single condensed nucleus  . Similarly, mass spectral evidence for polycyclic saturates suggests molecules with a condensed ring system at one end of a chain, but the interpretations are less clear and cannot yet exclude the possibility of ring systems at both ends. It appears that lubricating oil molecules may have short branches at the opposite ends of the long chain.

It is not the authors' intention to present this new picture of composition as a firmly established fact; instead, this paper represents an accumulation of ideas and conclusions which have been drawn from the interpretation of the mass spectra of a wide variety of narrow, heavy petroleum concentrates over a period of several years. Although the isolated data presented do not provide conclusive evidence, the combined mass spectral data point so strongly in the direction of a regular pattern of structural simplicity that it seems desirable to present the picture in its present form for others working in the field of oil constitution to consider. Although it is recognized that there is probably a small percentage of complex molecules, the authors consider the new picture to be one which, in general, is representative of the distillate range of petroleum ($<C_{40}$).

EXPERIMENTAL EVIDENCE

The experimental mass spectral evidence which furnishes the background for this new picture of structural composition is given below. Further information derived from other physical property data and from petroleum processing studies is being found which is consistent with the mass spectral picture, but, for the most part, its inclusion is beyond the scope of the present paper.

One of the major steps in the development of the

* MS received 22 January 1959. Presented in part at the 131st American Chemical Society Meeting, Miami, 11 April 1957.

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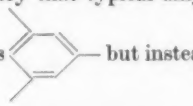
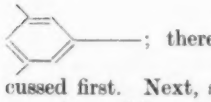
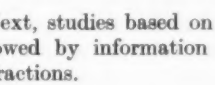
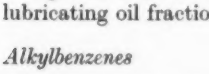
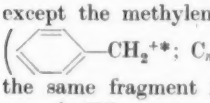
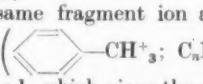
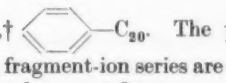
‡ Houston Research Laboratory, Shell Oil Company, Houston, Texas, U.S.A.

picture was the discovery that typical alkylbenzenes could not be depicted as  but instead must be  ; therefore, the alkylbenzenes are discussed first. Next, studies based on paraffin waxes are given, followed by information obtained from lubricating oil fractions.

Alkylbenzenes

The first mass spectra of lubricating oil-range petroleum fractions and pure compounds were run about nine years ago.[10] Mass spectra of pure mono-*n*-alkylbenzenes () were found to contain just a few major spectral peaks: (*a*) a parent-ion peak ( ; C_nH_{2n-6}); (*b*) a fragment-ion peak due to the loss of all of the alkyl chain except the methylene group attached to the ring ( ; C_nH_{2n-7}); and (*c*) a peak due to the same fragment ion after accepting a hydrogen atom ( ; C_nH_{2n-6}). This is illustrated in Fig 1, which gives the mass spectrum of *n*-eicosylbenzene,†  . The peak heights for the C_nH_{2n-7} fragment-ion series are indicated by circles in this and subsequent figures.

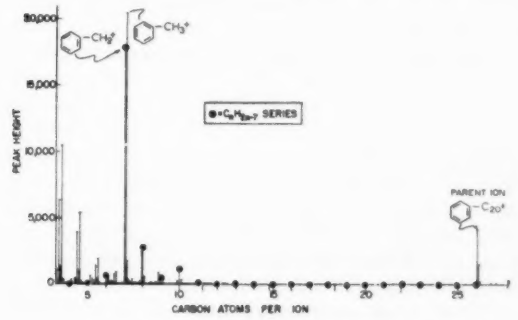
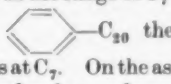
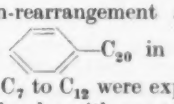


FIG 1

MASS SPECTRUM OF *n*-EICOSYLBENZENE

This information from pure alkylbenzenes was used to help interpret the first mass spectrum of a mono-aromatic concentrate (40 per cent alkylbenzenes) from a medium-viscosity lubricating oil distillate. A portion of this spectrum (the C_nH_{2n-7} series, which contains primarily fragments from alkylbenzenes) is shown in Fig 2. The peaks for the most abundant C_nH_{2n-7} fragment ions appear in the range of C_7 to C_{12}, whereas in Fig 1 for pure  the only appreciable C_nH_{2n-7} ion peak is at C_7. On the assumption that poly-substituted molecules undergo fragmentation and hydrogen-rearrangement somewhat similar to that of pure  in the mass spectrometer, the ions at C_7 to C_{12} were explained as major fragments from molecules with one to six alkyl substituents, respectively.

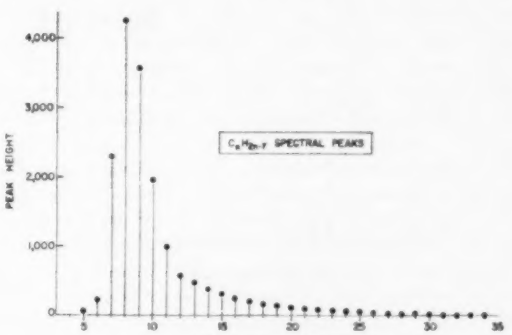
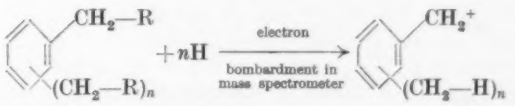
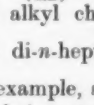


FIG 2

PARTIAL MASS SPECTRUM OF LUBRICATING OIL BENZENES



This explanation was in agreement with infra-red spectrometry data, which showed: (*a*) that the "average molecule" contained about three alkyl substituents, and (*b*) that the methylene groups were predominantly in chains of four or more.

The first mass spectra of pure dialkylbenzenes of the type R— —R soon exploded the idea of several long alkyl chains per benzene ring. The spectrum of di-*n*-heptylbenzene, C_7—  —C_7 ‡ (Fig 3), for example, shows that the major C_nH_{2n-7} fragment peak is not in the C_7–C_{12} range as in the narrow fraction of Fig 2, but instead it is at C_{14}, due to the loss of C_6 from one alkyl substituent. Thus, although in heavy petroleum fractions the average number of alkyl substituents on the benzene ring is about three, the first pure di-substituted benzenes

* Meyerson [9] has suggested that the major fragment ion is a tropylium ion, instead of the benzyl ion shown.

† Synthesized by API Research Project 42, Pennsylvania State University.

‡ Synthesized by Koninklijke/Shell-Laboratorium, Amsterdam.

proved to be less typical than the mono-substituted benzenes. That raised the question of how typical the spectrum of a synthetic tri-substituted benzene would be. To check the point a tri-substituted

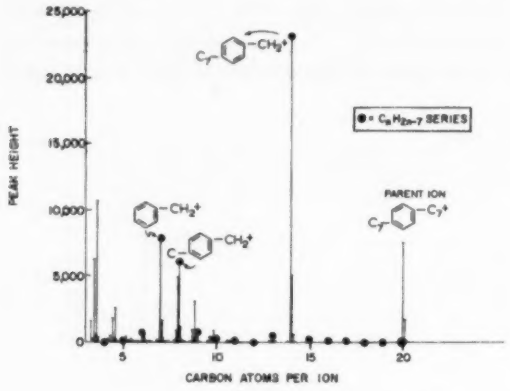
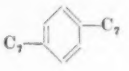
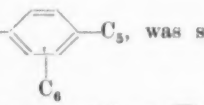


FIG 3

MASS SPECTRUM OF 1,4-DIHEPTYLBENZENE, 

benzene  , was synthesized and, as expected, its mass spectrum (Fig 4) looked nothing like that of the narrow lubricating oil fraction (Fig 2).

In the meantime, mass spectra of pure compounds of other hydrocarbon types had shown the great

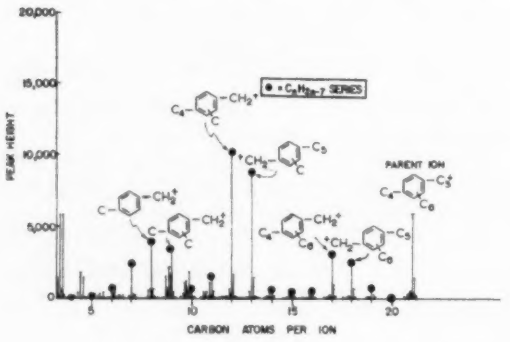
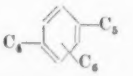
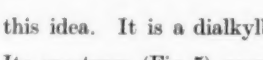
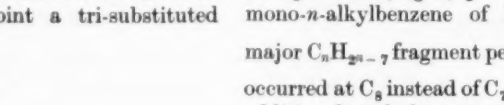


FIG 4

MASS SPECTRUM OF A TRIALKYLBENZENE, 

difficulty of losing any methyl group under electron bombardment in the mass spectrometer. This helped to provide a new concept of the nature of the alkyl substituents of the typical alkylbenzene from lubricating oil: one substituent must be a long-chain alkyl group, while the rest are methyl (and possibly ethyl) groups. Since that time, one pure compound of that general type has become available for testing this idea. It is a dialkylbenzene,  . Its spectrum (Fig 5) proved to be like that of the mono-*n*-alkylbenzene of Fig 1, except that the major C_nH_{2n-7} fragment peak  occurred at C_8 instead of C_7. Thus, it can be seen that additional methyl groups on the ring simply shift the major C_nH_{2n-7} fragmentation peak to higher carbon numbers until a maximum carbon number of 12 is obtained. This line of reasoning explains quite satisfactorily the mass spectrum of Fig 2 as resulting from a mixture of alkylbenzenes with one long-chain substituent and zero to four methyl substituents.

It is of interest to look at this picture of high-mass alkylbenzenes in the light of data on the natural

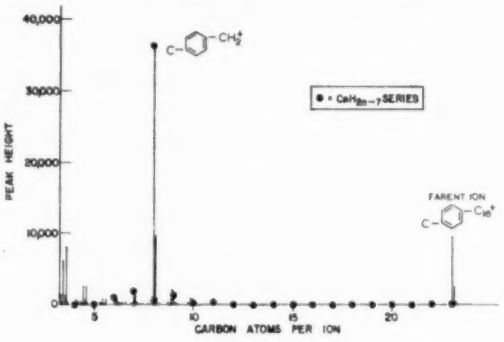
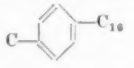


FIG 5

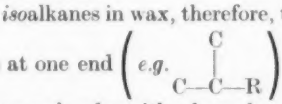
MASS SPECTRUM OF 1-METHYL-4-HEXADECYLBENZENE, 

abundance of the lower-boiling isomers. The data of Rossini *et al* [13] show the following distribution of C_9 alkylbenzenes in a Ponca City crude oil: 61 per cent trimethyl, 26 per cent methylethyl, and 13 per cent propyl. This is in agreement with the C_9 alkylbenzene data of Williams,[16] which showed 57 per cent, 32 per cent, and 11 per cent, respectively, for an unspecified crude. Williams also reported the following natural distribution for C_{10} alkylbenzenes: 5 per cent tetramethyl, 28 per cent dimethylethyl, 35 per cent methylpropyl, 12 per cent diethyl, and 20 per cent butyl. These data suggest a tendency for methyl substitution and no more than one long-chain substituent. Thus, these data from the gasoline range appear to be consistent with the high-mass picture of a benzene ring with one long-chain substituent and zero to four methyl substituents.

Paraffin Waxes

Although there are appreciable amounts of *iso*-alkanes and *cyclo*alkanes (as well as small amounts of aromatics) in paraffin waxes, the major component type is usually the *n*-alkanes. Thus, it seems logical

to assume that the non-*n*-alkane molecules present in wax are those which resemble most closely the *n*-alkanes in structure.

Of the *iso*alkanes in wax, therefore, those with short branches at one end  would be more likely than molecules with a branch near the centre or with branches at both ends. This has actually been shown to be the case by the combination of distillation, urea extractive crystallization, and mass spectrometry. Mass spectra of narrow distillation fractions from a wax of 122°–124° F melting point showed that the lengths of alkyl branches near the end of a chain varied from C_1 to about C_4, but that the average branch length did not vary appreciably with molecular weight. That the branching occurred only at one end was shown by the fact that virtually all the *iso*-alkanes reacted with urea to form a solid adduct. These spectral interpretations are in agreement with the conclusion of Sachanen [14] that the solid branched-chain alkanes of petroleum waxes are "slightly branched, for instance, with one or two methyl groups in the side chains," and with the conclusion of Warth [15] that "the branched chain contains but one carbon atom and is located near one end of the main chain."

Similarly, by distillation, urea extractive crystallization, and mass spectrometry, the *cyclo*alkanes in a refined wax were found to be predominantly mono*cyclo*alkanes with the ring attached to one end of the chain. If branching had occurred near the opposite end of the chain, fragment peaks due to the loss of the short alkyl branches would have been apparent on the C_nH_{2n-1} mass spectral series, and also such a molecule would not have been expected to react easily with urea. If branching had occurred on the carbon atom attached to the *cyclo*alkane ring, the mass spectrum would have shown the easy loss of the ring, with resulting large spectral peaks on the C_nH_{2n+1} and C_nH_{2n} series. Thus, the typical *cyclo*alkane in a wax must be a single ring with one long straight chain (and possibly one or two methyl substituents on the ring).

Attempts have been made to establish the relative abundances of *cyclo*hexyl and *cyclo*pentyl rings in waxes and other saturate fractions. A method [2] based on low-mass fragmentation peaks (C_4–C_{11}) has given a *cyclo*pentyl/*cyclo*hexyl ratio of about 50/50 for various paraffin waxes. However, the method would be expected to classify methyl-substituted *cyclo*-pentanes as *cyclo*hexanes. Thus, the true *cyclo*pentyl/*cyclo*hexyl ratios are probably higher than the experimental data indicate, and therefore it was concluded that the saturated rings in a wax are predominantly *cyclo*pentanes.

Lubricating Oil Saturate Fractions

Some of the most useful narrow fractions for the study of the structure of heavy petroleum molecules were prepared from the lubricant portion of a Ponca City, Oklahoma, crude oil by API Research Project 6.[12] Six of these fractions—five saturates and one aromatic—were submitted to various laboratories for co-operative spectrometric study [7] based on infra-red, ultra-violet, and mass spectra. Although the samples are not as nearly homogeneous with respect to ring number and carbon number as had been anticipated, they are still narrow enough for some important elements of molecular structure of typical hydrocarbon types to be established. For example, the molecular weight spread is narrow enough to show [11] that the mono*cyclo*alkanes in the lubricant fraction, like those in wax, have no appreciable branching on the carbon atom attached to the ring. Also, the *iso*-alkanes were shown to contain branches which are only slightly longer than those of wax *iso*alkanes. It appears that the lubricating oil molecules may contain, in addition to a ring system or branch at one end of the long alkyl chain, a short branch at the opposite end of the chain. In spite of the high melting points associated with long alkyl chains, such molecules would be expected to occur in low pour point oils because of the melting point depression due to the branching, the multiplicity of substitution on the ring systems, and the co-existence with other isomers in the mixture.

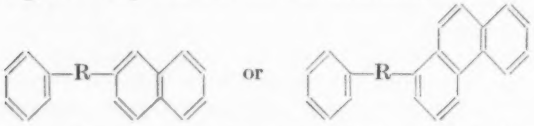
One interesting bit of infra-red information from the above co-operative spectrometric study serves as supporting evidence for the idea that mono*cyclo*-alkanes, like benzenes, have only one long-chain substituent but zero to five methyl groups on the ring. Infra-red data from S. A. Francis of the Texas Company [3] show that for the "average" mono*cyclo*-alkane in the API Project 6 saturate samples, predominantly all of the methylene ($-CH_2-$) groups of the alkyl substituents are in chains of six or more. This was based on the fact that the methylene-sequence absorption maximum was near 13·86 microns for all of the API samples. Instead of following the customary procedure of interpreting this to mean that all alkyl substituents contain seven or more carbon atoms, Francis concluded (on the basis of the average number of carbon atoms per molecule, the average number of substituents per molecule, and the average number of paraffinic methylene groups per molecule) that "there are a number of short chains contributing only a few paraffinic methylene groups and that most of these groups are contained in a few long alkyl chains." Thus, these conclusions, based on infra-red spectral data, point in the direction of fewer long chains and more methyl substituents than previously thought; and the experimental data are certainly consistent with the mass spectral picture that all substituents but one are methyl (and possibly ethyl) groups.

Condensation of Rings

Up to this point, the discussion of the experimental evidence and background has been concerned solely

with hydrocarbons containing no more than one ring per molecule. For hydrocarbons containing two or more rings per molecule the question arises as to whether the rings form a nucleus at one end of the chain (condensed) or whether such nuclei may occur at both ends of the chain (non-condensed or di-nuclear).

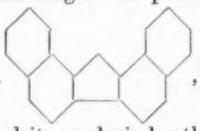
From a careful chromatographic separation of an East Texas medium lube distillate,[1] mass spectral evidence was found to indicate the occurrence of little, if any, non-condensation of aromatic rings. For example, fragment peaks typical of alkylbenzenes were found only in the monoaromatic region of the chromatogram, not in the tri- or tetra-aromatic region as they would be for the occurrence of



polynuclear types. The same situation exists for typical alkylnaphthalene fragment peaks. Thus, it must be concluded, at least for crudes similar to East Texas, that in refinery distillate streams the aromatic rings of the typical polyaromatic molecule all occur in a single condensed nucleus. It is of interest to note that Kurtz [4] has come to the same conclusion on the basis of the observed decrease in viscosity upon hydrogenation of lubricating oil aromatics. The conclusion is further substantiated by Rossini *et al* [12] from the increase in the number of hydrogen atoms per molecule on hydrogenation. The non-condensed configuration would require two more hydrogen atoms per molecule for complete hydrogenation.

In multi-ring saturated hydrocarbons the difficulty in obtaining mass spectral evidence for or against ring condensation is that their ring systems are much less stable towards electron bombardment in the mass spectrometer than are aromatic rings. In non-condensed ring systems one nucleus of condensed rings may be broken off from another. More confusing, however, is the fact that, contrary to the aromatic ring systems, a nucleus of condensed saturated rings can be broken apart to give fragments with fewer rings than in the original condensed nucleus. This peculiar type of fragmentation can lead to erroneous conclusions with regard to the number of condensed rings relative to the total number of rings per molecule. For example, in petroleum saturate concentrates a seemingly logical, but possibly erroneous, approach is to compare the small number of rings per nucleus shown by fragments with the larger number of rings per molecule shown by parent peaks and to define the difference as being due to the breaking of one condensed ring system from another.

Recent publications [5,8] have reflected an attempt to take this typical but confusing fragmentation into account. Lumpkin [5] has made a particularly noteworthy attempt to account for the fragmenting of condensed rings in his analytical method for distinguishing among molecules containing nuclei of two to six condensed saturated rings on the basis of mass spectral fragmentation peaks. He applied the method to the above-mentioned one-ring to three-ring saturate concentrates of API Project 6,[7] and the analyses for the average number of condensed rings per nucleus showed remarkably good agreement with the values determined for total rings per molecule by various other methods. These results indicated that molecules with three or less saturate rings contain predominantly a single nucleus of condensed rings. This is consistent with the fact that of the few pure di- and tri-*cyclo*alkanes isolated from the gasoline and kerosine range of petroleum, all are condensed-ring compounds.[6]

The authors have applied the Lumpkin method to several saturate concentrates containing four or more rings per molecule. For each concentrate the number of condensed rings per nucleus (Lumpkin fragment method) was compared with the total number of rings per molecule (parent-peak method). From this comparison the four-ring concentrates were shown to have essentially all four rings in a single condensed nucleus, but five-ring saturate concentrates were shown to contain relatively few five-condensed-ring nuclei. The tendency for molecules with five or more rings to appear non-condensed by the Lumpkin method may be due to the lack of calibration compounds containing five or six rings.[5] A pure five-condensed-ring hydrocarbon,  , has recently become available,* and its analysis by the Lumpkin method is as follows:

Condensed Rings	%
2	39
3	1
4	29
5	31

Although this compound may not be typical of lubricating oil penta*cyclo*alkanes, the analysis does bear out the authors' belief that the best available analytical method for studying ring condensation gives far too much evidence for non-condensation in molecules with five or more saturated rings.

Thus, the overall mass spectral evidence for multi-ring saturates points strongly in the direction of a single nucleus for one-ring to four-ring molecules. The evidence for non-condensation of rings in mole-

* Synthesized by API Research Project 42, Pennsylvania State University.

cules with five or more rings is questionable, so at present there is no proof either for or against the possibility of condensed saturate-ring systems at both ends of the main alkyl chain in those cases.

Similarly, for molecules containing both aromatic and saturate rings, it is possible that, in some cases, condensed ring systems occur at both ends of the alkyl chain. However, even in such cases the aromatic rings are expected to occur in a single condensed nucleus.

If, as discussed above, there is probably a single condensed nucleus in all cyclic compounds (both aromatic and saturate) which have two, three, or four saturated rings per molecule, only those molecules with five or more saturated rings per molecule could have nuclei at both ends of the main alkyl chain. Table I gives the mass spectrometric compositional data for the overhead material from a molecular distillation of West Texas straight-run residue and shows that only about 5 per cent of the molecules (excluding resins) contain five or more rings per molecule. Thus, only a small number of molecules in the sample could be so complex as to have nuclei at both ends of the main alkyl chain. This composition is approximate and would be expected to vary from one crude to another, but it does serve to emphasize the extent to which simple molecules actually occur in petroleum.

TABLE I

Composition of Overhead Material from Molecular Distillation of West Texas Straight-Run Residue

No. of saturated rings/molecule	Composition, %				
	Saturates	Mono-aromatics	Di-aromatics	Other poly-aromatics	Total
0	12·5	4·3	3·3		
1	19·5	4·4	4·1		
2	8·0	3·7	3·6	11·0 *	91·0
3	5·4	2·5	2·4		
4	3·7	1·4	1·2		
5+	4·0	0·6	0·5	—	5·1
	53·1	16·9	15·1	11·0	96·1 †

* No accurate means of distinguishing saturate ring numbers.

† The remainder is "resin."

Non-Hydrocarbons

Although the above discussion has been concerned with hydrocarbons alone, mass spectral data indicate that the non-hydrocarbons also are relatively simple in structure. A thiophene or pyrrole ring, for example, can be considered simply as replacing a benzene ring in the above discussion of aromatic hydrocarbons.

CONCLUSIONS

It has long been considered that the more we know about the composition of petroleum, the more direct our approach can be to research on such aspects as the origin, migration, and refining of petroleum. The mass spectrometric picture of structure of high-boiling petroleum molecules presented in this paper not only provides additional information on composition but at the same time suggests that the structural composition is actually much simpler than has been anticipated.

ACKNOWLEDGMENTS

The authors wish to express their gratitude to E. G. Carlson for his general contribution to this publication, to M. L. André for the analysis of the West Texas straight-run residue, to I. Dvoretzky, W. H. Hinds, and R. H. Hunt for the synthesis of the tri-alkyl benzene, and to C. J. Busso and the late A. A. Schaerer for the narrow fractions from wax.

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OBITUARY

JEAN LOUIS EUGÈNE GROFF

1893–1959

JEAN GROFF, whose death on 23 February is announced with much regret, was well known in the petroleum industry and particularly in the lubrication field.

Born on 3 April 1893, he entered the Institut Industriel du Nord de la France in Lille in 1910, and four years later took his engineer's degree, gaining second place out of 120 graduates and being first in the electricity section. He also gained the prize awarded by the Société Industrielle du Nord.

Serving in the first world war, he was wounded at Verdun and held as a prisoner-of-war until January 1919. He received the Croix de Guerre.

His early career from 1910 began in iron and steel and then in the chemical industry. His first introduction to lubrication was in 1927, when he joined the Société des Huiles Galéna and, when the Company was taken over by The Texas Company, Jean Groff played an important part in its expansion. Later he became chief engineer of its Technical Department when it changed its name to Société des Raffineries de Pétrole de la Gironde (now Caltex S.A.F.).

During the second world war, Jean Groff was seconded to the Office Central de la Répartition des Produits Industriels, and then to the Comité d'Organisation des Combustibles Liquides. For his services he was awarded in 1944 the Gold Medal of the Société d'Encouragement pour l'Industrie Nationale.

After the war he was placed in charge of the Lubricants Department of the Institut Français du Pétrole and was also lecturer on lubrication in numerous technical schools and training establishments. His previous experience in the study of lubrication made him well fitted to take the lead in the creation and development of the Lubricants Department and its establishment in the new laboratories at Rueil-Malmaison.

During the period 1951–55, he contributed to the *Revue de l'Institut Français du Pétrole* a condensation of his teachings and experience. Entitled "l'ABC du Graissage," this received favourable world-wide criticism and has been accepted as an authoritative work on lubrication.

A member of many technical societies, including the Institute of Petroleum since 1937, Jean Groff will be missed by his many friends throughout the world. His upright character and unfailing kindness endeared him to all who met him, and his technical ability will be a great loss to the science and practice of lubrication.

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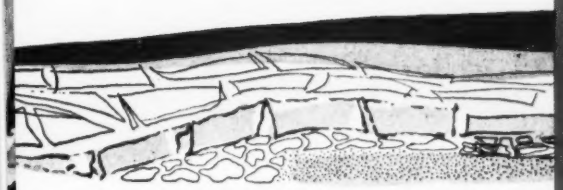

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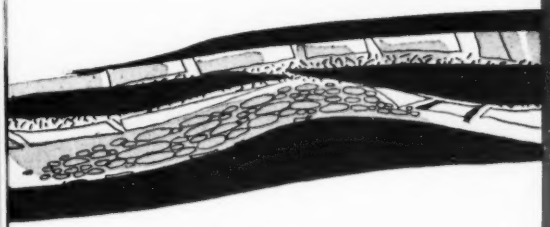

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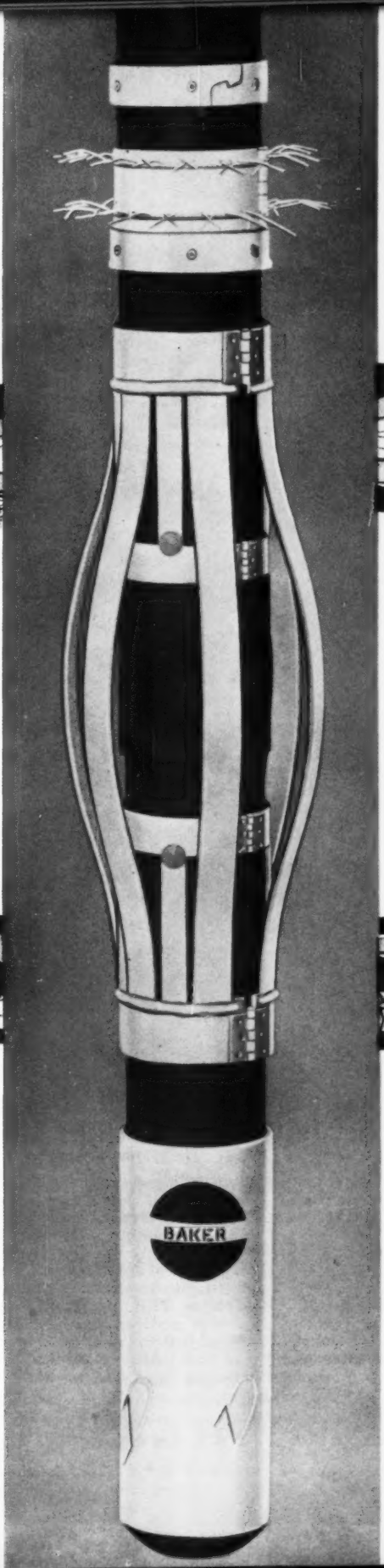

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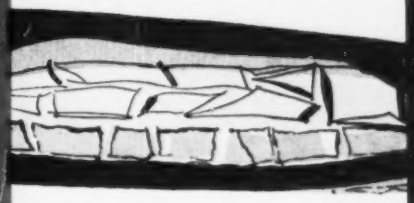

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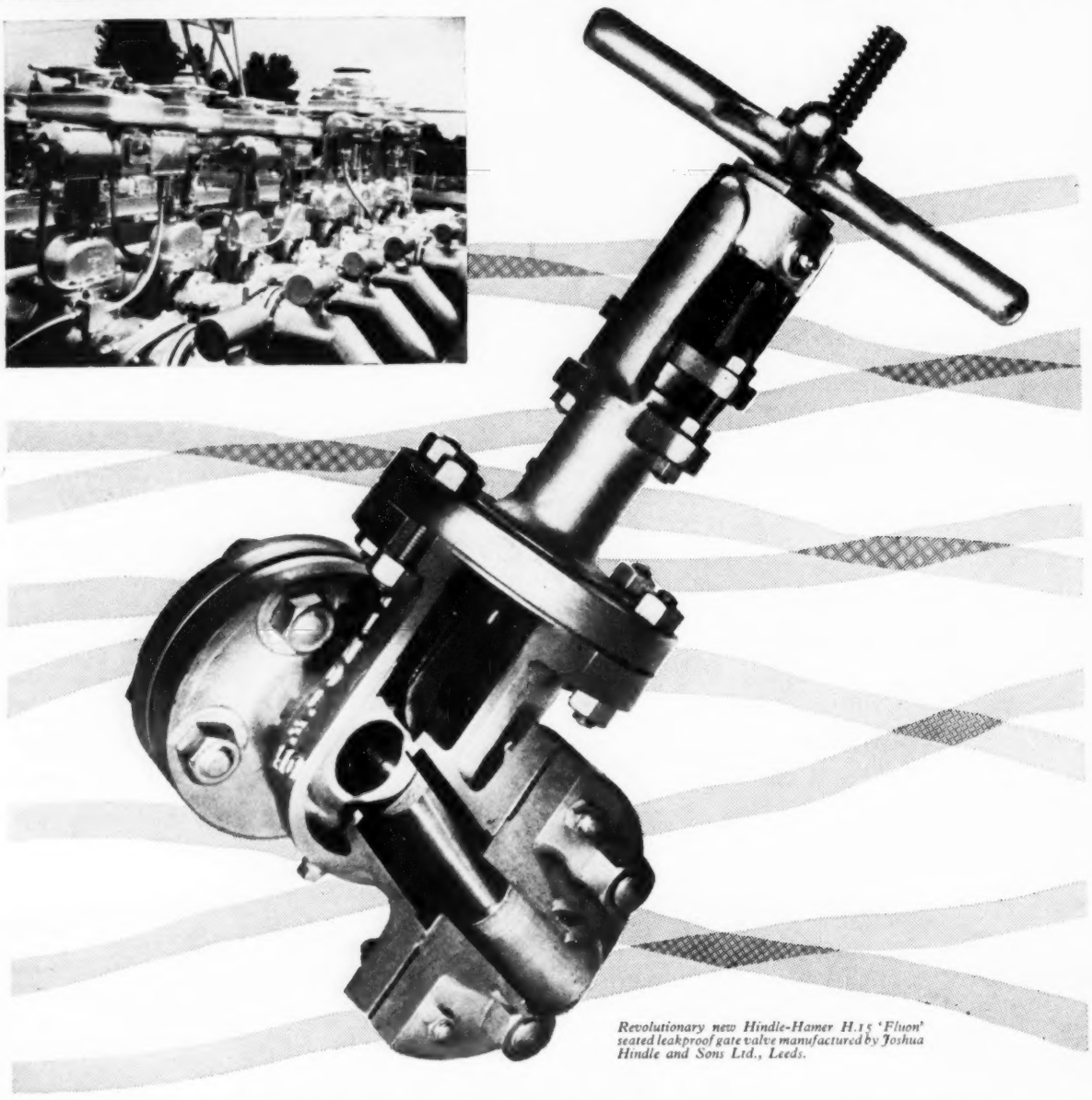

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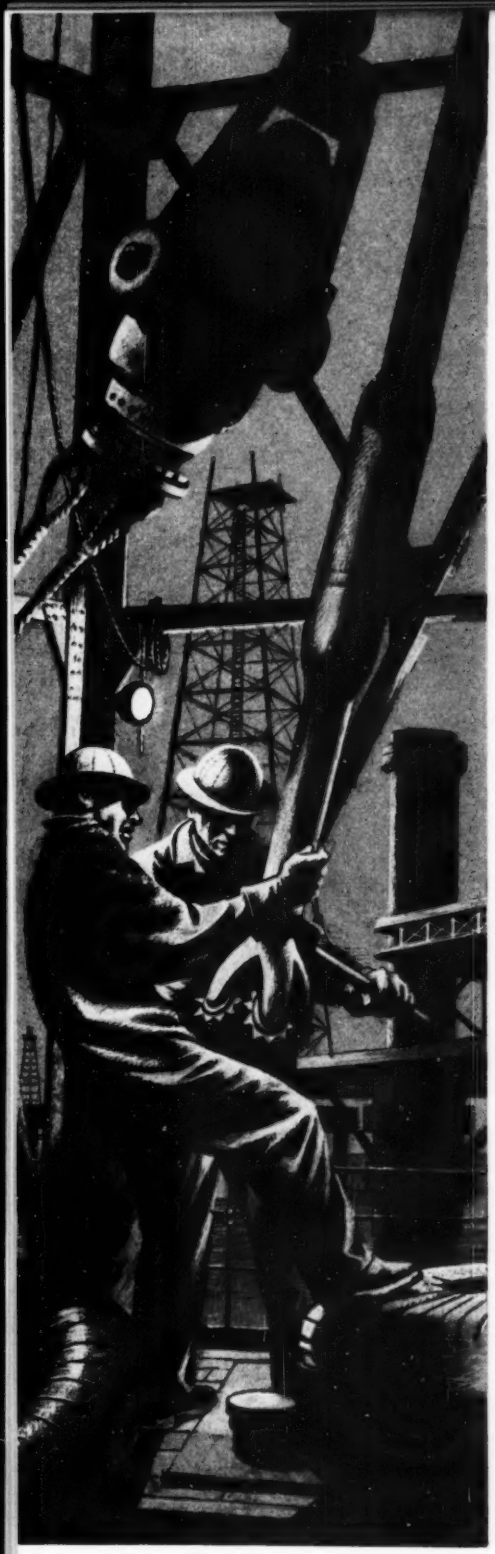

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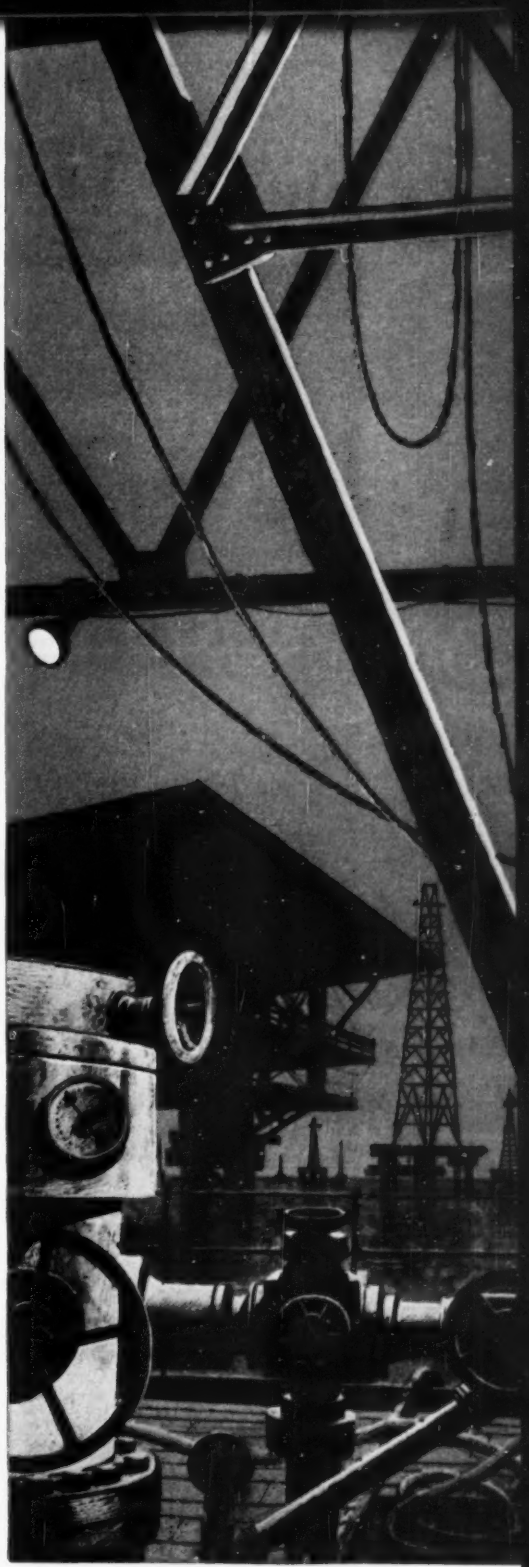

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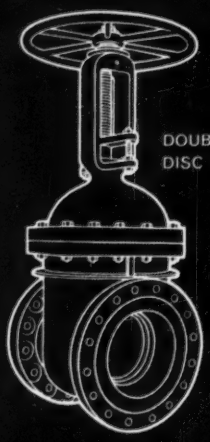

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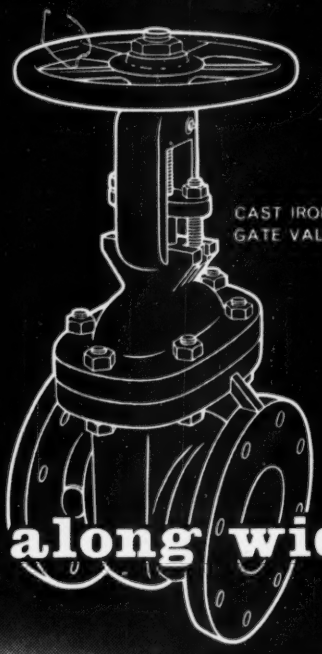

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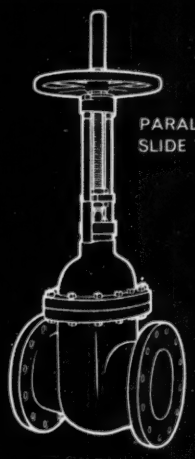

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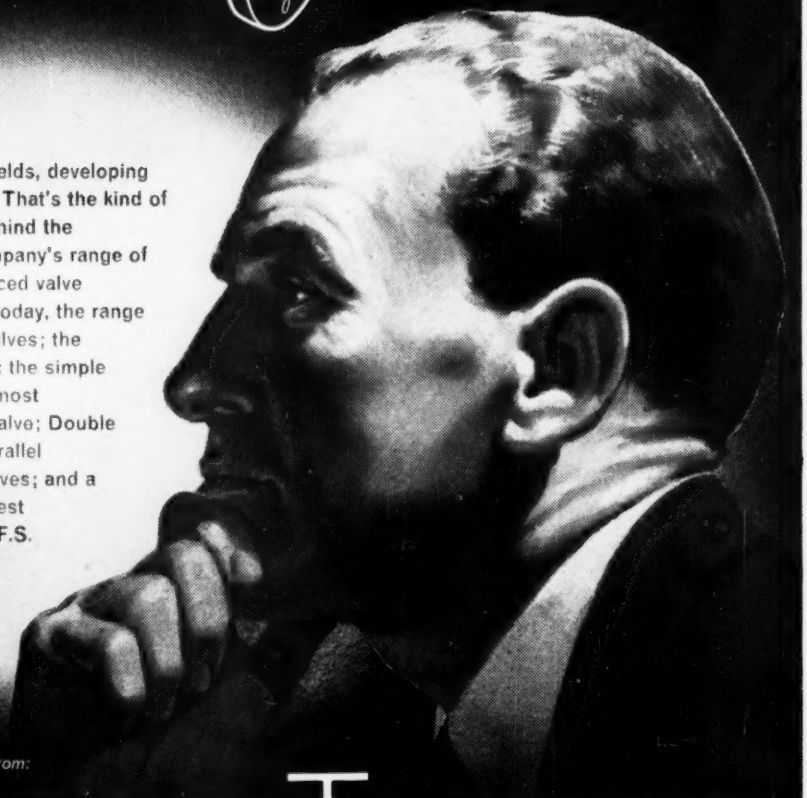

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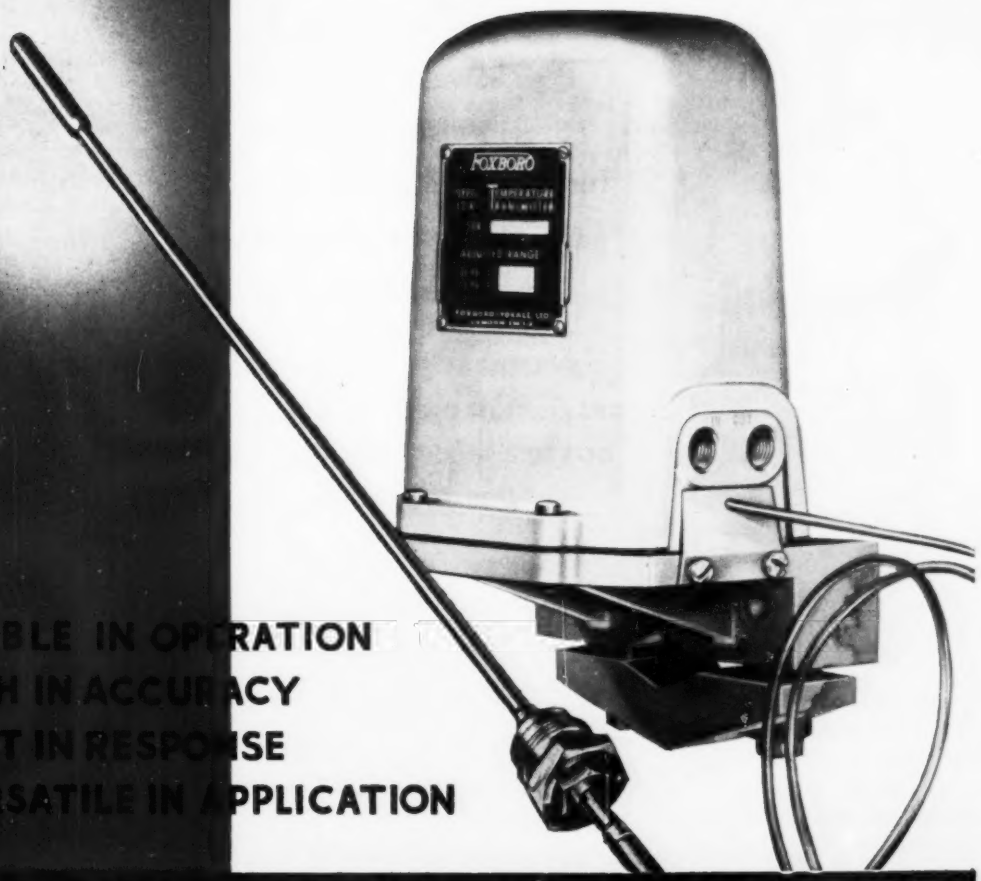

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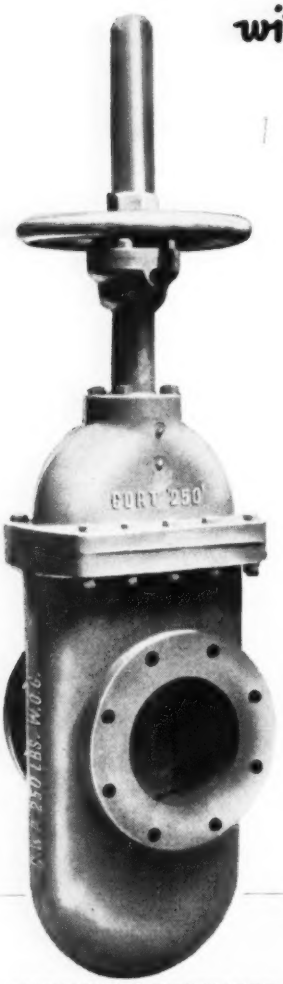

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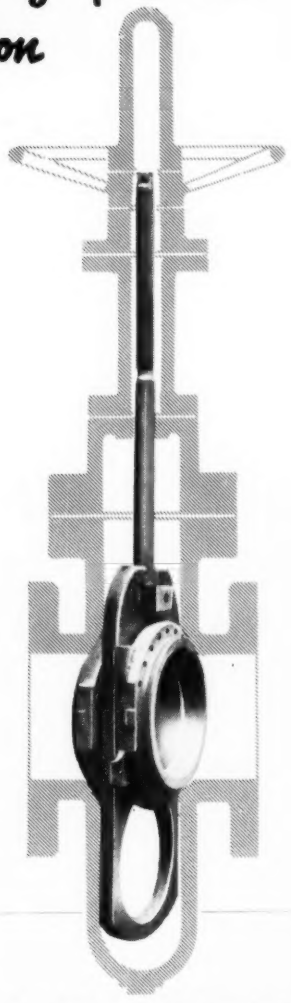

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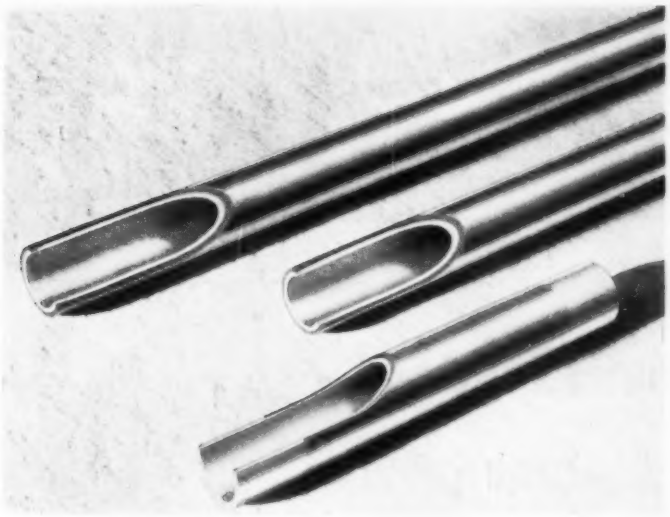

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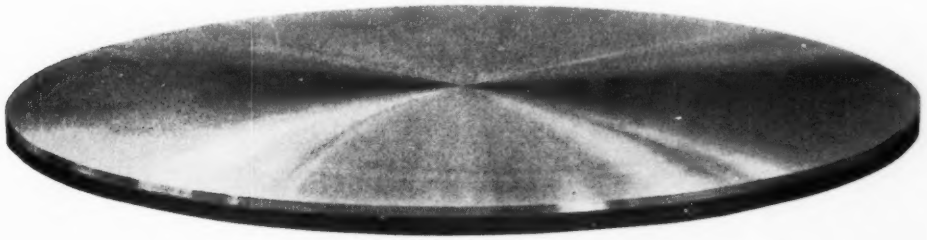

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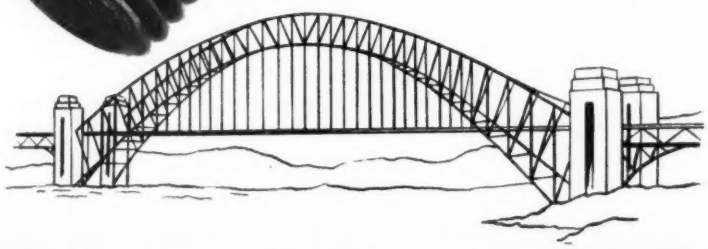

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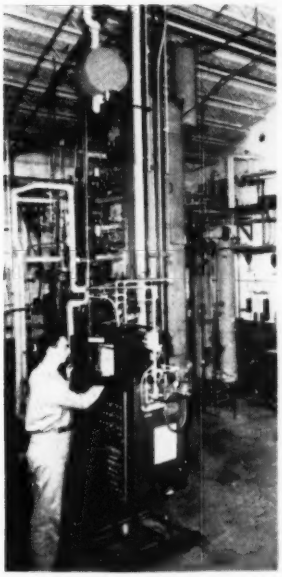

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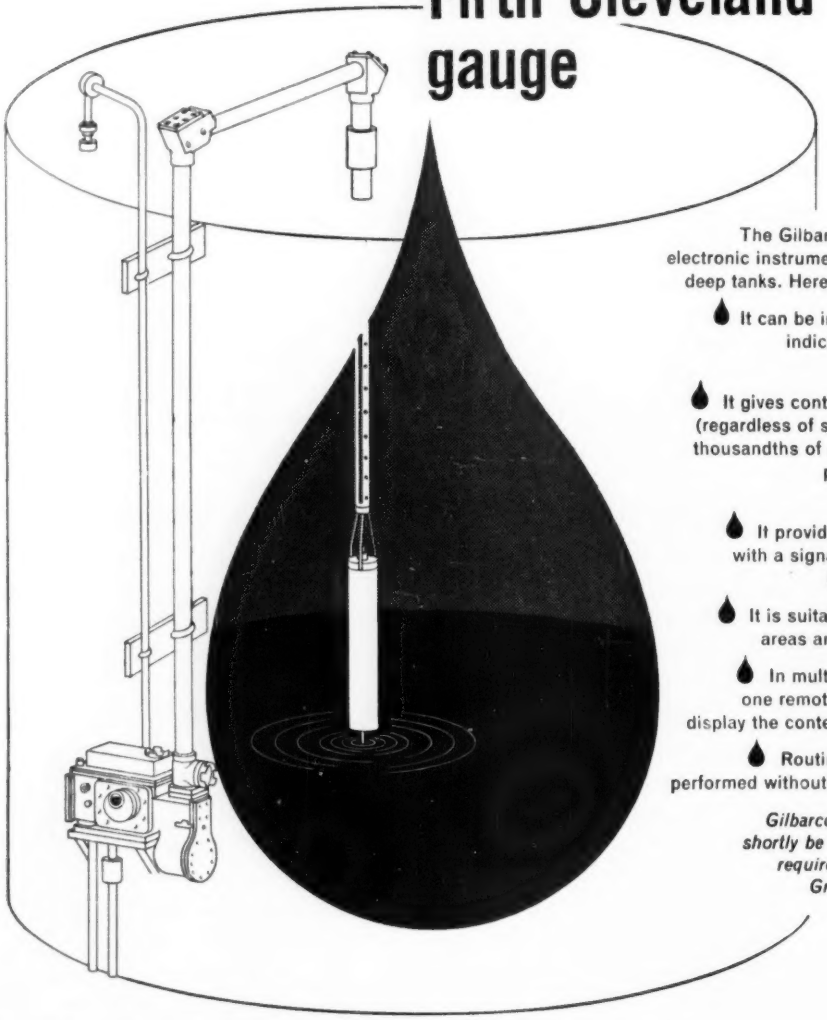
this is the GILBARCO Firth Cleveland gauge



The Gilbarco Gauge is a highly accurate electronic instrument for indicating liquid level in deep tanks. Here are a few of its advantages:—

- It can be installed in tanks of all types to indicate liquid level or the interface between two liquids.
- It gives continuous readings of liquid level (regardless of specific gravity) to within a few thousandths of an inch of height—a feature of particular importance for tanks with large surface areas.
- It provides local and remote indication with a signal to operate data reduction or logging equipment if required.
- It is suitable for operation in hazardous areas and in extremes of temperature.
- In multiple storage tank installations, one remote indicator can be arranged to display the contents, in turn, of up to 50 tanks.
- Routine maintenance can be readily performed without taking the tank out of service.

Gilbarco Gauges of our production will shortly be available to Buxton flame-proof requirements or to American Class 1, Group D, Division 1 classification

Made under licence to Gilbert and Barker Mfg. Co., U.S.A For full details write to:

FIRTH CLEVELAND INSTRUMENTS LTD

TREFOREST · PONTYPRIDD · GLAMORGAN **A MEMBER OF THE FIRTH CLEVELAND GROUP** FC

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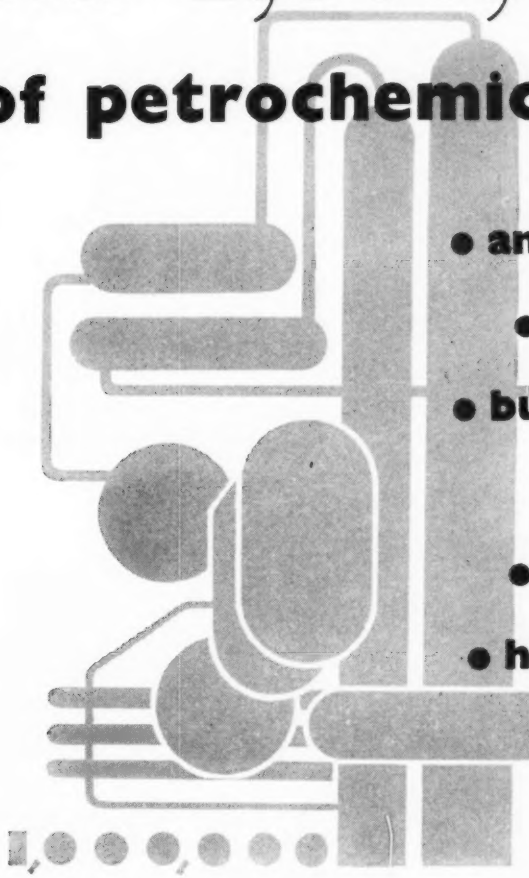
over 1,000,000 tons/yr.

of petrochemical know-how



- ammonia
- butadiene
- butyl rubber
- ethylene
- dodecyl benzene
- hydrogen
- methanol
- urea

More than twenty FW process installations totalling more than a million tons capacity per year are now in operation or under construction. This specialized know-how—encompassing design, engineering, fabrication and erection all over the world—gives Foster Wheeler a firm foundation for serving the requirements of all producers planning process facilities in the expanding petrochemical industry.

FW

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158 ton fusion welded tower for Fawley

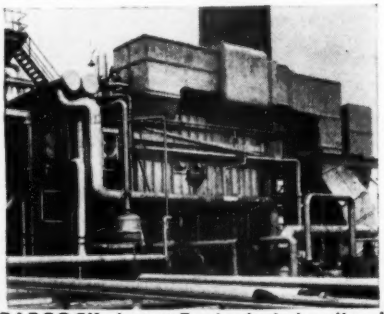
Shown below, in transit to the Esso Refinery, Fawley, is a 105-ton section of a 158-ton, 137 ft.-high stabilising tower fabricated by BABCOCK fusion-welding, to the order of the Lummus Co. Ltd., for Esso Petroleum Co. Ltd.

BABCOCK

Equipment for the Oil and Chemical Industries

Babcock & Wilcox Ltd. is outstandingly well equipped in experience, techniques and manufacturing facilities to meet the demands of the oil and chemical industries for complete steam-raising plants, pressure vessels (in mild-steel or clad plate), separately-fired superheaters, heat exchangers and waste-heat utilization plant.

Many of the world's largest pressure-vessels have been Babcock fusion-welded, including the giant heat-exchangers of Britain's first atomic power stations and a large number of treating towers for the world's oil refineries and chemical plants. The Company has, indeed, an exceptional experience of fabrication by fusion-welding and as the world's largest maker of steam-raising plant, has a thorough understanding of the principles and problems of heat-exchange.



BABCOCK plant at Fawley includes oil and gas fired boiler plant. Above: one of the outdoor type FH Integral Furnace boilers.

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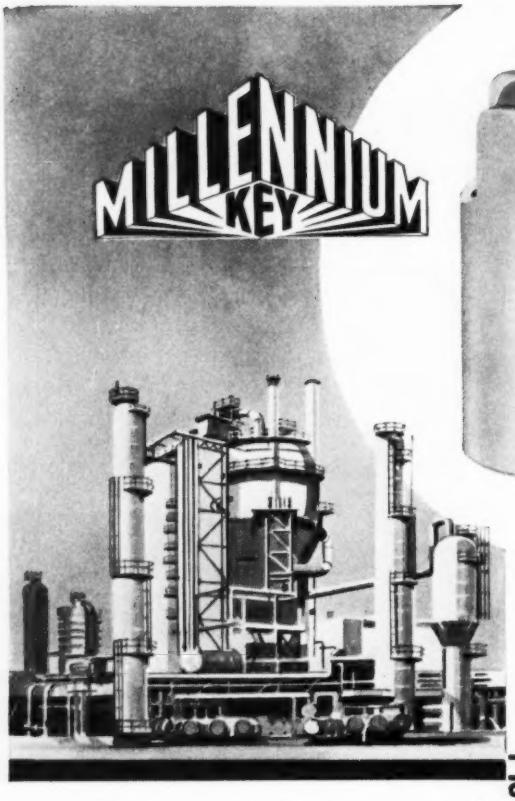

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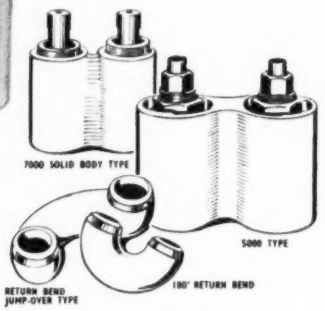
highest quality fittings for refinery and chemical plants



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Procon (Great Britain) Ltd

The Procon (Great Britain) Ltd advertisement on page ii of the April issue of the *Journal* carried a footnote which implied that F. A. Trim was the London representative for the company.

This footnote should have appeared with the Universal Oil Products Company's advertisement on page xix of the issue.

It is much regretted that this error occurred.

intangibles were never so important

VISIONEERED PROCUREMENT

Procuring the innumerable items for construction of a petroleum, chemical or petrochemical plant is a complex undertaking requiring a high degree of experience and foresight. Working in close coordination with estimating, engineering, drafting, field construction, inspection and expediting personnel, the Procon purchasing staff provides many intangible services of inestimable value. This is another reason why a Procon-built plant is economical in cost, completed on time and superior in performance!

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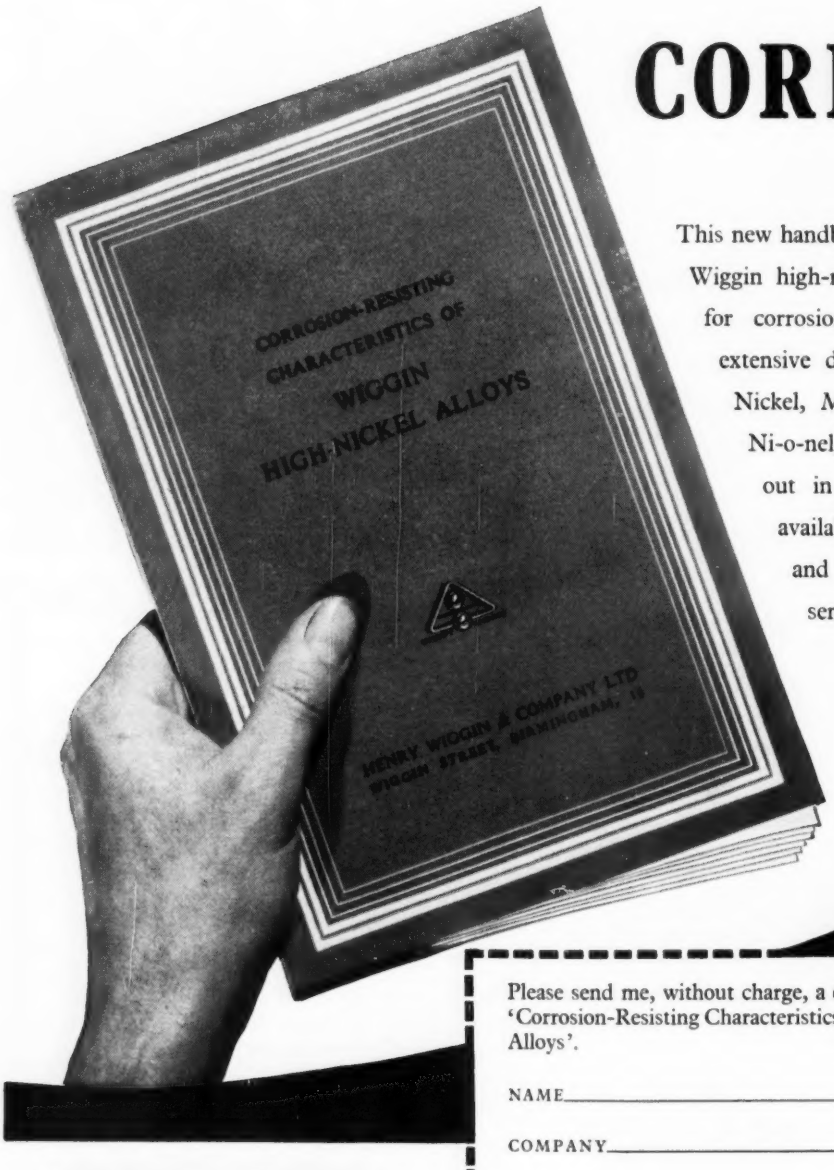
Knowing where to find the answers on

CORROSION



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HOLD IT!

WITH SIMMONDS FLOW CONTROL VALVES

Simmonds Flow Rate Control Valves

Simmonds Flow Rate Controllers are designed to limit the liquid stream automatically to a specified rate of flow. They are basically plug valves, their progressive opening and closing being governed by the differential pressure developed across an orifice placed in the fuel stream—this pressure being a function of the flow rate. Valves are available for capacities of 100/800 i.g.p.m.

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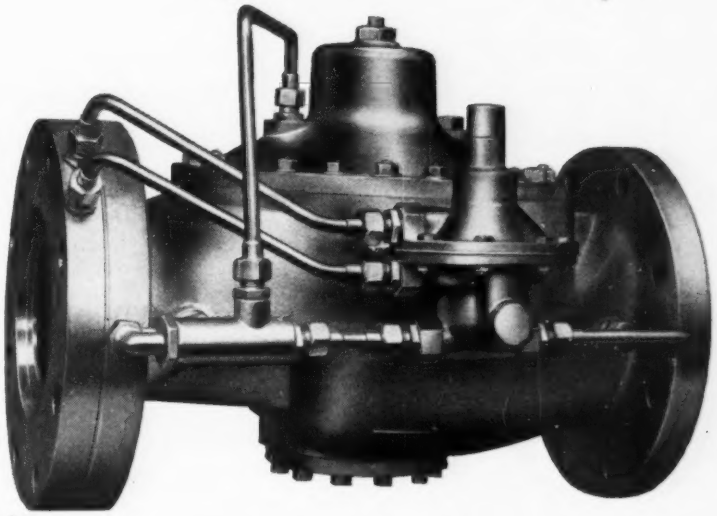
When the flow rate of liquid exceeds a predetermined value, these Simmonds valves will immediately operate to shut off the flow. Once the flow has been stopped, it can only be resumed by manually re-setting the valves, which will handle rates of flow within an overall range of 100/800 i.g.p.m.

These Flow Control Valves are subjected to stringent tests in the Firth Cleveland Test House at Treforest. Proving their function under controlled conditions ensures that performance is always up to specification.



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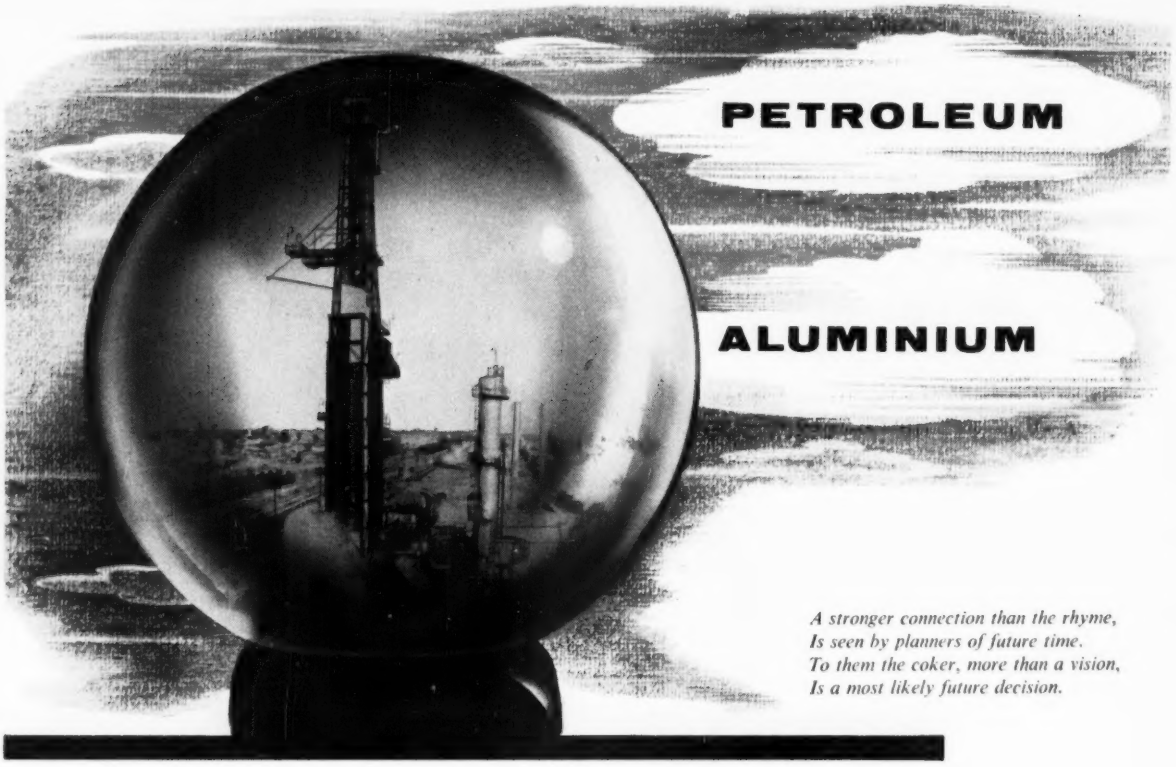

A stronger connection than the rhyme,
Is seen by planners of future time.
To them the coker, more than a vision,
Is a most likely future decision.

Looking into the future petroleum refiners can be expected to make petroleum coke for the expanding of British and European aluminium companies. To make a pound of aluminium requires half a pound of coke in the form of electrodes. Throughout the world the aluminium industry prefers to use coke made from petroleum by the delayed coking process rather than coke made from coal because of the latter's high ash content. During the last sixteen years the Kellogg organisation has on the average designed, engineered and constructed one delayed coking unit per year. The wealth of experience culminating from this continuing engineering programme to design and build better delayed coking units is available through the Kellogg International Corporation. Oil refining companies concerned with future planning are invited to discuss the economic and technical aspects of delayed coking or of any other refining process with the Kellogg International Corporation.

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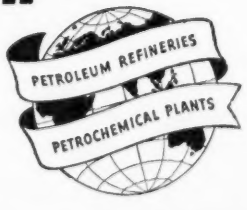
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